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# Dimephosphone Analogs: I. Synthesis and Structure of Some Dimephosphone Aryl- and Acylhydrazones

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**Abstract**—Dimephosphone (2-dimethoxyphosphoryl-2-methylpentan-4-one) phenyl-, nitrophenyl-, benzoyl-, and 4-nitrobenzoylhydrazones were synthesized. The compounds in crystals were shown to have a steric form exclusively of the *E*-isomer. The structure of hydrazones in solution is defined by the nature of the substituents and the solvent and the time of storage of the solution. The dimephosphone aroylhydrazones in acid solutions exist in several possible forms: the isomers at the imine bond, the conformers at the amide bond, and a cyclic tautomer (1,3,4-oxadiazoline).

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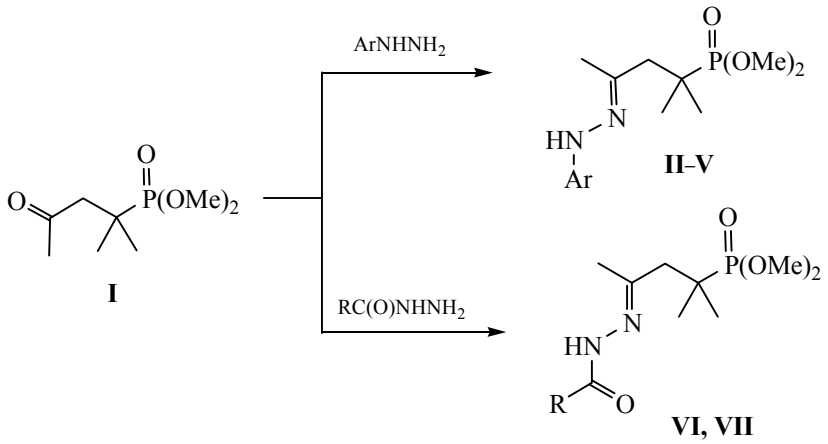
Aqueous solutions of 2-(dimethoxyphosphoryl)-2-methylpentane-4-one [dimethyl (2-methyl-4-oxopentan-2-yl)phosphonate], more known as dimethyl 1,1-dimethyl-3-oxobutylphosphonic acid (**I**) are used as a dimephosphone drug, which has a wide range of applications in medicine [1–3].

The dimephosphone belongs to organophosphorus compounds. Unlike most of the used organophosphorus compounds, it does not exhibit anticholinesterase activity and is even recommended as an antidote at the poisoning by toxic products. The dimephosphone has been used since 1973 as an antiacidotic means at the acidosis of various etiologies, a vasoactive drug in the treatment of cerebral circulation disfunction and respiratory diseases. The drug exhibits membrane-stabilizing and anti-inflammatory properties. At the external use it exhibits an antiseptic effect, enhances the protective function of the skin and mucous membranes. The dimephosphone was found to have also cardiotropic, neurotrophic, neuroprotective, antihypoxic, antiallergic, immunocorrection, antiaggregation, antioxidant, and radioprotective properties. This drug improves blood circulation and normalizes metabolic processes in the brain tissue. The dimephosphone was proposed for the treatment of autoimmune thyroiditis, gastric and duodenal ulcer, purulent sinusitis, and other diseases [1, 2].

The dimephosphone is a bright example of the successful pursuit of drugs among the organophosphorus compounds. By its chemical nature, the dimephosphone belongs to γ-phosphorylated ketones and therefore it is of interest as a precursor in the synthesis of new potential biologically active compounds. Along with other approaches, the principle of analogy with the known drugs is widely used in pharmacology. Despite the great synthetic chemical potential of the dimephosphone as a ketone, its chemical properties, in contrast to pharmacological ones, have been poorly studied [1]. Among its derivatives only the dimephosphone oxime is described [4, 5]. The aim of this work was the synthesis of some dimephosphone aryl- and acylhydrazones that might be of interest as objects of theoretical and structural chemistry, and as biologically active compounds and precursors in the synthesis of heterocyclic systems (indoles, oxadiazoles, triazoles, etc.).

The dimephosphone arylhydrazones **II–V** and aroylhydrazones **VI, VII** unknown previously were obtained in the classical way [6]: by the reaction of the corresponding hydrazine derivative in alcohol with dimephosphone along the scheme below (see the Experimental and Table 1).

The synthesized dimephosphone arylhydrazones, including phenylhydrazone **II**, are crystalline colored




Ar = Ph (**II**), 4-$O_2NC_6H_4$ (**III**), 2-$O_2NC_6H_4$ (**IV**), 2,4-$(O_2N)_2C_6H_3$ (**V**); R = Ph (**VI**), 4-$O_2NC_6H_4$ (**VII**).

substances. The color depends on the position rather than the number of the nitro groups: light beige crystals of phenylhydrazone **II** (almost white after reprecipitation from methanol with water), pale brown 4-nitrophenylhydrazone **III** and orange 2-nitro- **IV** and 2,4-dinitrophenylhydrazones **V**. Deeper color of the two latter compounds is presumably due to the presence in their molecules of a strong intramolecular hydrogen bonds of $NO_2\cdots HN$ type involving the nitro groups in *ortho*-positions to the hydrazone fragment [6]. The hydrogen bonding in the hydrazone molecules was confirmed by X-Ray analysis.

The stability of dimephosphone arylhydrazones **II–V** depends strongly on the nature of the aryl substituent and the storage conditions. At storage in air even in a closed vessel the dimephosphone phenylhydrazone crystals soon turn red (in 1–2 days). They gradually gutter, turning first into a dark red, then dark brown resinous mass. This process occurs even faster at elevated temperature (in 12–15 h) and in solution, especially in chloroform. At storage in a dark brown closed bottle the changes occur in 30–35 days. Because of this we failed to grow a crystal suitable for the X-ray analysis.

We fixed by IR spectroscopy the presence of dimephosphone in the products of the spontaneous decomposition of phenylhydrazone **II**. Such behavior is typical of the phenylhydrazones of aliphatic and cycloaliphatic ketones and arylhydrazones containing donor substituents in the arene ring [6, 7]. These transformations are not related to tautomeric transformations into the azo compounds, which have been sometimes postulated up to now [8], but result from the oxidation processes. It has been already found long ago [6, 7] that similar arylhydrazones readily form by the mechanism of ene reaction the azohydroperoxides of the ArC(OOH)–N=N–Ph type, which decompose spontaneously in the reaction medium. This leads to

**Table 1.** Some characteristics of dimephosphone arylhydrazones **II–V** and acylhydrazones **VI, VII**

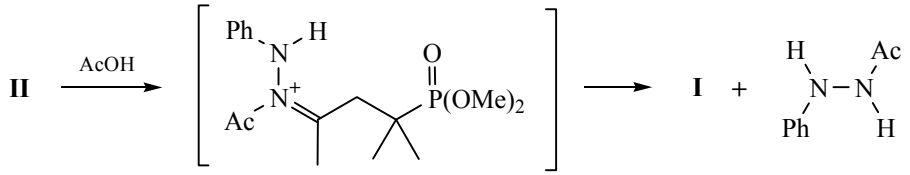
| Comp. no. | Yield, % | mp, °C | IR, ν, $cm^{-1}$ | | Found, % | | | | Formula | Calculated, % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | NH | C=N | C | H | N | P | | C | H | N | P |
| **II** | 61 | 114–118 (decomp.) | 3265 | 1599 | 56.46 | 7.86 | 9.55 | 10.28 | $C_{14}H_{23}N_2O_3P$ | 56.37 | 7.77 | 9.39 | 10.38 |
| **III** | 88 | 193–194 | 3272 | 1613 | 48.53 | 6.63 | 12.41 | 9.28 | $C_{14}H_{22}N_3O_5P$ | 48.98 | 6.46 | 12.24 | 9.02 |
| **IV** | 37 | 65–66 | 3328 | 1616 | 48.49 | 6.37 | 12.30 | 8.65 | $C_{14}H_{22}N_3O_5P$ | 48.98 | 6.46 | 12.24 | 9.02 |
| **V** | 75 | 121–121.5 | 3327 | 1615 | 43.43 | 5.57 | 14.38 | 8.08 | $C_{14}H_{21}N_4O_7P$ | 43.30 | 5.45 | 14.43 | 7.98 |
| **VI** | 90 | 144–146 (decomp.) | 3219 | 1615 [ν(C=O) 1673] | 55.04 | 7.22 | 8.62 | 9.28 | $C_{15}H_{23}N_2O_4P$ | 55.21 | 7.10 | 8.58 | 9.49 |
| **VII** | 83 | 161–163 | 3232 | 1604 [ν(C=O) 1668] | 48.66 | 5.81 | 11.24 | 8.47 | $C_{15}H_{22}N_3O_6P$ | 48.52 | 5.97 | 11.32 | 8.34 |

the formation of diverse products, including carbonyl compounds corresponding to the ylidene fragment of the parent hydrazone. It was proved that a mysterious change in the color of benzaldehyde phenylhydrazone observed during its storage in the light, at transfer in the darkness and back again, also is due to such oxidative processes rather than to the change in the geometry of the hydrazone group [9]. Perhaps these processes underlie the fact that the only known analog of the dimephosphone phenylhydrazone, the diethyl (2-methyl-4-oxopent-2-yl)phosphonate phenylhydrazone, was characterized not as a crystalline substance, but as a dark brown liquid [10].

The ability of the phenylhydrazone **II,** which is prone to autoxidation, to remain unchanged for three months or more at keeping in water is surprising.

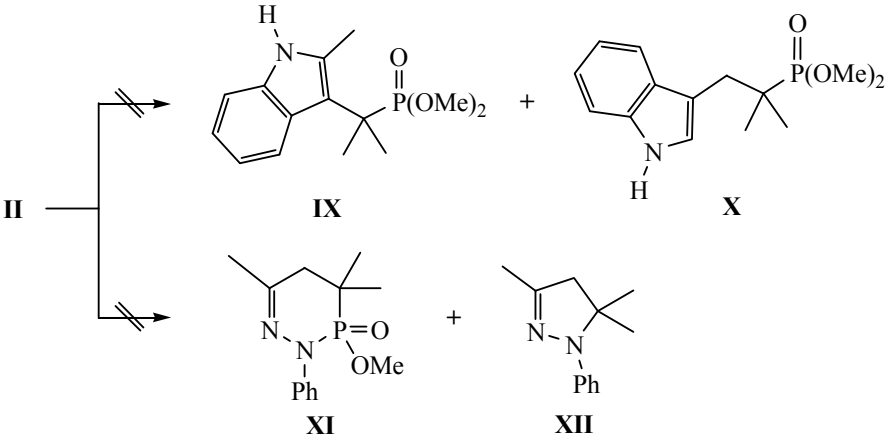
Introduction of nitro groups in the benzene ring stabilizes the dimephosphone phenylhydrazone molecule. Crystals of 2-nitrophenylhydrazone **III** are changed only in 3–3.5 months, and the crystals of 4-nitro- **IV** and 2,4-dinitrophenylhydrazones **V** can be kept for more than three years without any changes.

Despite numerous attempts, we were not able to perform indolization of nitrophenylhydrazones **III, IV** or even phenylhydrazone **II**. The attempted reaction in acidic medium (hydrochloric acid of different concentrations, polyphosphoric acid, etc. [6], a mixture of hydrochloric acid and AcOH [11]), in most cases yielded the dimephosphone and arilhydrazine salts. After boiling phenylhydrazone **II** in glacial AcOH for 3 h the acetic acid phenylhydrazide was isolated nearly quantitatively, while 4-nitrophenylhydrazone **III** remained unchanged at boiling in AcOH for a longer time. In the aliphatic ketone phenylhydrazones, including the phenylhydrazone **II**, the most basic nitrogen atom is the imine nitrogen of the hydrazo group [12]. Therefore, in glacial AcOH the phenylhydrazone acylation can proceed at this atom, and the resulting hydrazonium salt of the type **VIII**, as is well known [6], is readily hydrolyzed to the corresponding phenylhydrazide. The introduction of a nitro group in the benzene ring of such phenylhydrazones significantly reduces their basicity, and the most basic center in nitrophenylhydrazones takes another position.




**VIII**

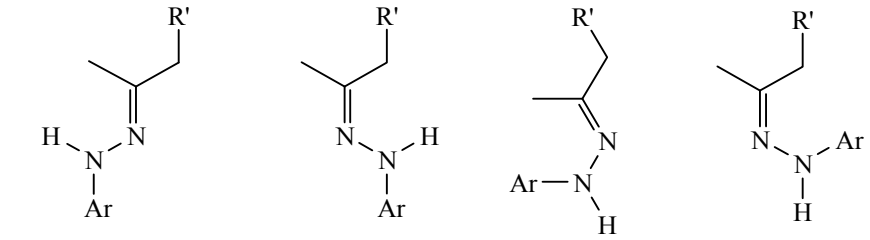
According to GLC, prolonged (25 h) boiling of phenylhydrazone **II** in toluene or xylene leads to the reaction products containing no methanol, and the isolated liquid is dimephosphone. This fact indicates that at the thermolysis neither indolization reaction proceeds to form **IX** or **X**, nor intramolecular phosphorylation at the amino group of hydrazone fragment occurs giving diazaphosphorinane **XI** derivatives, nor dimethyl phosphite cleavage with subsequent cyclization of intermediate mesityl oxide phenylhydrazone into the corresponding pyrazoline **XII**, but only take place the processes of oxidative destruction.




**IX** **X**

**XI** **XII**

Theoretically, the asymmetrically substituted ketone arylhydrazones, including dimephosphone, can exist as four flat steric forms due to different positions of the fragments relative to the C=N double bond ($E_{C=N}$ and $Z_{C=N}$ isomers, further for the convenience denoted as *E*- and *Z*-isomers) and relative to the N–N bond ($E'_{N–N}$ and $Z'_{N–N}$ conformers, further *E*'- and *Z*'-conformers). The N–N bond is not a single bond due to *n*–*p*-conjugation [6]. However, its double-bonding order determined mainly by the nature of the substituents in the aryl fragment is not high enough to restrict significantly the internal rotation around this bond. The introduction of nitro groups in the benzene ring redistributes the electron density in the arylhydrazone fragment even more reducing the N–N bond order [6, 13, 14]. Therefore, the $Z'_{N–N}$ conformers of the hydrazones of various types are generally not realized due to steric hindrances [6, 7], and therefore *EZ*'- and *ZZ*'-conformers are not considered in this paper.




$E_{C=N}$, $E'_{N-N}$ (*E*,*E*') *Z*,*E*' *E*,*Z*' *Z*,*Z*'

R' = $CMe_2P(O)(OMe)_2$.

According to IR spectra, the dimephosphone arylhydrazones **II–V** exist in the crystals in a single form (Table 1). The presence in the IR spectra of the absorption bands corresponding to only one N–H bond and the absence of absorption bands belonging to the multiple C=C bonds show the presence of the arylhydrazone tautomers and the absence of the enehydrazine forms. Apparently, the location of the acceptor dimethoxyphosphoryl group in the γ-position to the imine fragment does not contribute to the stabilization of the latter, although one it is possible to detect a small amount of enol form in the dimephosphone [1]. The less strong absorption of the N–H bond of dimephosphone phenylhydrazone (Table 1) compared with crystalline sample of benzaldehyde phenylhydrazone (3315 $cm^{-1}$) and acetophenone phenylhydrazone (3350 $cm^{-1}$) [15] can be attributed to its participation in intermolecular N–H···O=P (or N–H···O–P) hydrogen bond with dimethoxyphosphoryl group.

In freshly prepared solutions of arylhydrazones **II–V** in $CDCl_3$, $CD_3CN$, and DMSO-$d_6$ also only one form was found. Over time, in the NMR spectra of the solutions the signals of the other form appear (Table 2), in the amount determined by the nature of the aryl substituent, the nature of the solvent, and the time interval between the preparation of the solution and recording the spectrum. The introduction of nitro groups in *ortho*-position of the benzene ring impedes the transformation of the original *E*-isomer into another (see Table 2). However, an unambiguous conclusion about the structure of the more stable form of arylhydrazones **II–V** basing on the data in these tables is difficult. One should take into account the possible stereochemical lability of dimethoxyphosphorylisobutyl fragment (several single bonds: P–C, C–C), which in many ways can determine the spatial requirements of the substituted methylene group compared with the methyl one. Therefore to obtain an unequivocal result we studied the structures of nitrophenylhydrazones **III–V** using X-ray diffraction analysis. We failed to grow a crystal of phenylhydrazone **II** suitable for X-ray study because of its propensity to oxidation. The geometry of molecules of nitrophenylhydrazones **III–V** is shown in Figs. 1–3, and Tables 3 and 4 list their structural parameters. The data show that in all cases the crystals contain only $E_{C=N}$ isomers existing as the $E_{N–N}$ conformers, with noticeable difference in the stereochemistry of the phosphorylalkyl fragment.

Bond lengths and bond angles in the hydrazone fragment of the molecules of nitrophenylhydrazones **III–V** (Table 3) are close to those of the corresponding sterically non-hindered arylhydrazones [14, 16] and suggest the *p*–π-conjugation in the arylhydrazone fragment usual for such systems [6]. As a consequence, the bond order of the imine bond is reduced to ~1.9, and

**Table 2.** Principal parameters of $^{1}H$ and $^{31}P$–{1H} NMR spectra of dimephosphone arylhydrazones **II–V** and acylhydrazones **VI, VII**

$RNHN{=}C(Me)CH_2CMe_2P(=O)(OMe)_2$

| Comp. no. | R | Solvent | Form | Forms ratio, % | $^{1}H$, δ, ppm (*J*, Hz) | | | | | | | $^{31}P$, $\delta_P$, ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | >$CMe_2$ ($^{3}J$, d) | | =CMe | >$CH_2$ ($^{3}J$, d) | | OMe ($^{3}J$, d) | | NH | |
| **II** | Ph | $CDCl_3$[a] | *E* | 88 | 1.28 | (17.1) | 1.97 | 2.59 | (11.8) | 3.79 | (10.5) | 7.28 | 38.9 |
| | | | *Z* | 12 | 1.34 | (17.4) | 2.18 | 2.66 | (10.8) | 3.71 | (10.8) | 7.34 | 40.2 |
| | | $CD_3CN$ | *E* | >98 | 1.20 | (16.9) | 1.92 | 2.49 | (11.1) | 3.72 | (10.2) | 7.55 | 38.5[b] |
| | | DMSO-$d_6$ | *E* | >99 | 1.15 | (16.9) | 1.91 | 2.42 | (10.7) | 3.67 | (10.2) | 8.67 | 38.5 |
| | | $CF_3COOH$[c] | *E*+$H^+$ | 75 | 0.90 | (16.5) | 2.15 | 2.59 | (18.1) | 3.38 | (10.5) | –[c] | 35.4 |
| | | | *Z*+$H^+$ | 25 | 0.98 | (17.1) | 2.17 | 2.74 | (17.1) | 3.43 | (10.8) | –[c] | 38.3 |
| **III** | 4-$NO_2C_6H_4$ | $CDCl_3$[a] | *E* | 98 | 1.25 | (17.0) | 1.99 | 2.57 | (12.2) | 3.76 | (10.4) | 7.71 | 37.9 |
| | | | *Z* | 2 | 1.44 | (15.5) | 2.14 | 2.72 | (11.9) | 3.95 | (10.4) | –[d] | –[d] |
| | | $CD_3CN$ | *E* | >99 | 1.21 | (16.8) | 1.97 | 2.52 | (11.7) | 3.71 | (10.3) | 8.39 | 38.1 |
| | | DMSO-$d_6$ | *E* | >99 | 1.16 | (16.8) | 1.99 | 2.46 | (11.4) | 3.68 | (10.3) | 9.80 | 37.8 |
| | | $CF_3COOH$[a] | *E*+$H^+$ | 87 | 0.91 | (16.7) | 2.21 | 2.69 | (18.1) | 3.39 | (10.8) | –[c] | 34.7 |
| | | | *Z*+$H^+$ | 13 | 0.81 | (16.6) | 2.20 | 2.68 | (18.0) | 3.38 | (10.7) | –[c] | 38.1 |
| **IV** | 4-$NO_2C_6H_4$ | $CDCl_3$ | *E* | 100 | 1.38 | (17.0) | 2.07 | 2.64 | (11.7) | 3.79 | (10.4) | 10.66 | 37.9 |
| | | $CD_3CN$ | *E* | 100 | 1.22 | (18.8) | 2.03 | 2.57 | (11.7) | 3.72 | (10.3) | 10.50 | 38.6 |
| | | DMSO-$d_6$ | *E* | 100 | 1.18 | (16.8) | 2.06 | 2.54 | (11.2) | 3.69 | (10.3) | 10.44 | 39.2 |
| | | $CF_3COOH$[e] | *E*+$H^+$ | >90 | 0.89 | (16.8) | 2.25 | 2.73 | –[d] | 3.37 | (10.7) | 9.72 br.s | 36.7 |
| | | | *Z*+$H^+$ | ~5 | 0.96 | (18.2) | 2.28 | –[d] | –[d] | 3.56 | (10.7) | | 39.2 |
| **V** | 2,4-$(NO_2)_2C_6H_3$ | $CDCl_3$ | *E* | 100 | 1.28 | (17.8) | 2.15 | 2.67 | (12.6) | 3.79 | (10.5) | 11.02 | 37.3 |
| | | $CD_3CN$ | *E* | 100 | 1.24 | (16.7) | 2.13 | 2.62 | (11.3) | 3.72 | (10.3) | 10.87 | 37.4 |
| | | DMSO-$d_6$ | *E* | 100 | 1.20 | (16.8) | 2.07 | 2.59 | (11.4) | 3.70 | (10.3) | 10.78 | 38.1 |
| | | $CF_3COOH$[a] | *E*+$H^+$ | 86 | 0.90 | (17.3) | 2.08 | 2.69 | (16.2) | 3.41 | (10.8) | 10.29 | 37.0 |
| | | | *Z*+$H^+$ | 14 | 0.98 | (16.8) | 2.34 | 2.74 | (16.8) | 3.34 | (10.8) | –[d] | –[d] |
| **VI** | PhC(=O) | $CDCl_3$ | *EE'E"* | 56 | 1.31 | (16.1) | 2.13 | 2.46 | (18.4) | 3.68 | (10.6) | 10.98 | 37.0 |
| | | | *EE'Z"* | 44 | 1.24 | (18.4) | 2.09 | 2.59 | (10.6) | 3.71 | (10.5) | 9.01 | 38.4 |
| | | $CD_3CN$ | *EE'Z'* | >95 | 1.21 | (16.7) | 2.01 | 2.54 | (~16) | 3.68 | (10.2) | 9.02 | 38.3 |
| | | DMSO-$d_6$ | *EE'Z'* | >98 | 1.17 | (16.9) | 2.00 | 2.50 | (–[d]) | 3.69 | (10.2) | 10.46 | 38.7 |
| | | $CF_3COOH$ | Cycle | 41 | 0.74 | (18.2) | 1.67 | 2.21 | (13.3) | 3.25 | (10.9) | –[d] | 36.1 |
| | | | *EE'E"*+$H^+$ | 49 | 0.84 | (17.1) | 2.14 | 2.64 | (18.1) | 3.31 | (10.9) | –[d] | 38.4 |
| | | | *EE'Z"*+$H^+$ | 10 | 0.91 | (16.7) | 2.57 | 2.60 | (~16) | 3.28 | (10.8) | –[d] | 39.1 |
| **VII** | 4-$NO_2C_6H_4C(=O)$ | $CDCl_3$ | *EE'E"* | >90 | 1.35 | (16.1) | 2.18 | 2.50 | (18.8) | 3.47 | (10.6) | 11.50 | 39.5 |
| | | | *EE'Z"* | ~4 | 1.29 | (17.4) | 2.12 | 2.61 | (10.6) | 3.79 | (10.3) | 8.98 | 37.2 |
| | | $CD_3CN$ | *EE'Z"* | 80 | 1.22 | (17.4) | 2.08 | 2.57 | (12.2) | 3.72 | (10.9) | 9.40 | 38.2 |
| | | | *EE'E"* | 10 | 1.33 | (16.0) | 2.12 | 2.21 | (–[d]) | 3.70 | (–[d]) | 11.38 | 40.5 |
| | | DMSO-$d_6$ | *EE'Z"* | ~86 | 1.18 | (17.0) | 2.08 | ~2.5 | (–[d]) | 3.69 | (10.9) | 10.80 | 38.1 |
| | | | *EE'E"* | ~7 | 1.20 | (16.9) | 2.02 | –[d] | (–[d]) | 3.67 | (10.6) | 11.18 | 39.1 |

**Table 2.** (Contd.)

| Comp. no. | R | Solvent | Form | Forms ratio, % | $^1$H, δ, ppm (*J*, Hz) | | | | | $^{31}$P, $\delta_P$, ppm |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | >$CMe_2$ ($^3J$, d) | =CMe | >$CH_2$ ($^3J$, d) | OMe ($^3J$, d) | NH | |
| **VII** | 4-$NO_2C_6H_4C$(=O) | $CDCl_3$ | *Z E*′*Z*″ | ~7 | 1.24 (–[d]) | 1.96 | 2.63 (16.6) | ~3.55 (–[d]) | – | 37.4 |
| | | $CF_3COOH$ | **A** | ~42 | 0.78 (18.1) | 1.72 | 2.26 (13.0) | 3.30 (10.5) | – | 35.0 |
| | | | **B** | ~37 | 0.88 (16.7) | 2.19 | 2.70 (18.46) | 3.36 (10.9) | – | 37.6 |
| | | | **C** | ~7 | 0.96 (16.7) | ~2.6 | –[d] –[d] | 3.35 (10.6) | – | 40.0 |

[a] After 2 h the freshly prepared solution contains only the $E_{C=N}$.form. [b] For the second isomer (less that 5%), $\delta_P$ = 39.3 ppm. [c] The signals of NH group protons are not recordable due to exchange processes. [d] Not identified. [e] After 8 days the freshly prepared solution contained only one form, with admixture of the third form, δ($CMe_2$) 0.80 ppm (*J* ~ 18 Hz), δ(=CMe) 2.41 ppm, δ(OMe) 3.18 ppm (10.7 Hz), $\delta_P$ 35.6 ppm.

N–N and C–Ar bond orders increase to 1.2 and 1.5, respectively. The values of the bond angles involving the atoms of the hydrazone fragment in the studied nitrophenylhydrazones (Table 3) indicate the absence of a steric hindrance in this part of the molecules. It was previously shown that in the molecules of the sterically hindered arylhydrazones the value of, for example, the N–N=C bond angle, increased to 122–125° compared with 115–117° in the sterically unloaded derivatives (see [16] and Table 3).

In the molecules of the nitrophenylhydrazones **III–V** the carbon atoms of methyl and methylene groups of the ylidene fragment and the atoms of hydrazo group are located in the same plane *P*(1) [$N^1N^2C^2C^3C^4$]. The atom $C^1$ linked to the phosphorus atom and two methyl groups is in the same plane only in the molecules of 4-nitrophenylhydrazone **III** (see torsion angles in Table 3). This atom is in the *eclipsed* conformation with respect to the imine nitrogen atom $N^2$ [the torsion angle $N^2C^3C^2C^1$ is ~3°], its deviation from the *P*(1) plane is small and amounts to –0.036(3) Å. The methyl groups are located on both sides of this plane at nearly equal distances (Tables 3 and 4). In the molecules of 2-nitro- and 2,4-dinitrophenylhydrazones **IV, V** the $C^1$ atom is removed considerably from the *P*(1) plane [the $C^1$ atom deviations from the *P*(1) plane in the molecular crystals **IV** and **V** are –1.382(3) and –1.369(3) Å, respectively, see Table 4]. Dimethoxyphosphorylisopropyl fragment is turned around the $C^2$–$C^3$ bond in the same direction by 96° and 78°, respectively, in the molecules of compounds **IV, V**, which confirms our assumption on the stereochemical lability of the fragment. Moreover, in crystals of 2,4-dinitrophenylhydrazone **V** one of the methoxy groups of the dimethoxyphosphoryl fragment is disordered over two positions with occupancy ratio 0.62:0.38 (Fig. 3).

It is interesting to note that in the molecules of arylhydrazones **III–V** the benzene rings and nitro groups also lie in this *P*(1) plane. The rotation angles of the benzene rings relative to the *P*(1) plane and nitro groups relative to the plane of the benzene ring are small (see Table 3), which also indicates a large extent of delocalization (conjugation) of electronic systems of the aryl and hydrazone fragments.

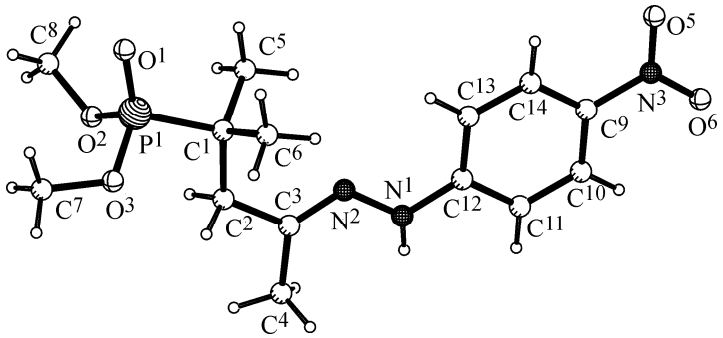



**Fig. 1.** Molecular geometry and numbering of atoms in the crystal of dimephosphone 4-nitrophenylhydrazone **III**.

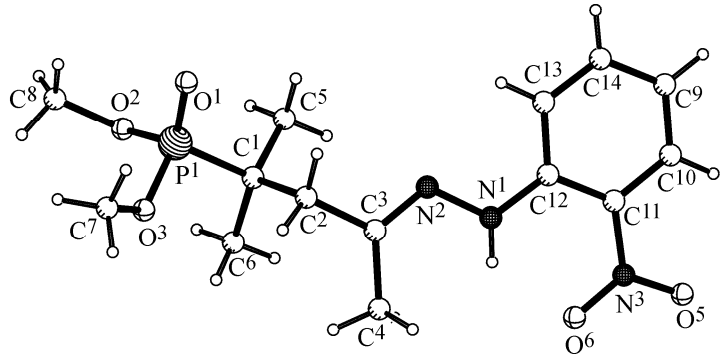



**Fig. 2.** Molecular geometry and numbering of atoms in the crystal of dimephosphone 2-nitrophenylhydrazone **IV**.

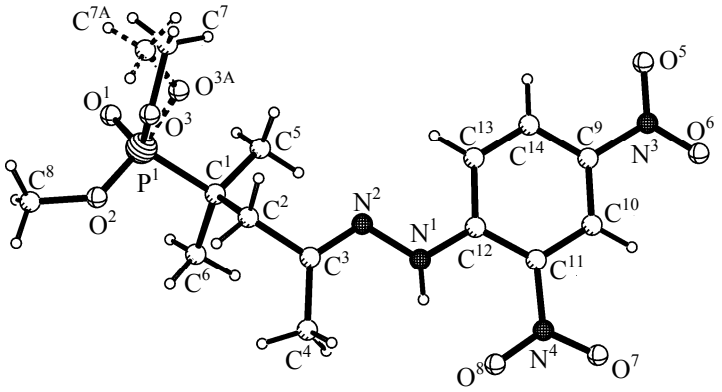



**Fig. 3.** Molecular geometry and numbering of atoms in the crystal of dimephosphone 2,4-dinitrophenylhydrazone **V**.

Analysis of the molecular packing of molecules of nitrophenylhydrazones **III–V** in crystals shows that the decisive role plays the nitro group position. Thus, in the crystal of 4-nitrophenylhydrazone **III** due to $N^1$–$H^1\cdots O^1$ intermolecular hydrogen bonding (Table 5) molecular chains are formed along the 0*y* axis (Fig. 4). In crystals of the arylhydrazones **IV, V** containing a nitro group in the *ortho* position of benzene ring are formed only the intramolecular $N^1$–$H^1\cdots O^6$ ($N^1$–$H^1\cdots O^8$) hydrogen bonds (Table 5, Figs. 3 and 4) typical of the *ortho*-nitroaniline derivatives [14].

In a crystal of 4-nitrophenylhydrazone **III** there are also short contacts of C–H···O=P type (Table 4), which stabilize additionally the molecular chains (Fig. 2, 1D). In crystals of arylhydrazones **IV, V** due to the same contacts the molecules form dimeric fragments, which in the crystal of **IV** form a belt along the 0*z* axis, and in the crystal of **V** they form a chain along the side diagonal of the *a*0*c* plane (Figs. 5 and 6, respectively).

The introduction of a carbonyl group between the aryl and hydrazone fragments greatly complicates the stereochemistry of the obtained aroylhydrazones. It was already repeatedly shown that, depending on the state of aggregation, the nature of substituents in the ylidene and acyl fragments, and the solvent, the acylhydrazones may exist in a variety of steric forms, or as mixtures of several forms [6, 7, 17–20], including the cyclic 1,3,4-oxadiazol-2-ine form [21]. It was previously considered that aldehyde acylhydrazones existed only in the form of the *E*-isomer with respect to the C=N double bond regardless of the nature of substituents at the amine nitrogen atom, while the acylhydrazones of the unsymmetrically substituted ketone could exist as two isomers about the double C=N bond [6, 7, 17]. However, it was shown by the method of infrared spectroscopy that acetyl- and benzoylhydrazones of symmetrically substituted ketones like acetone also existed in the solutions as two conformers due to another factor, the hindered internal rotation around the amide N–C bond [17]. Later on, using the methods of dipole moments, IR and $^1$H NMR spectroscopy it was revealed that arylaldehyde aroylhydrazones in crystal and in solution are mixtures of two amide forms, $E_{C=N}$, $E_{N-N}$, $E_{N-C}$ and $E_{C=N}$, $E_{N-N}$, $Z_{N-C}$ (further for convenience, *EE'E"* and *EE'Z*") [18]. The possible formation of intramolecular

**Table 3.** Selected geometric parameters of the dimephosphone aryl- and aroylhydrazones **III–VII** molecules

| Parameter | III | IV[a] | V[b] | VI | VIIA | VIIB |
|---|---|---|---|---|---|---|
| | | | Bond length, Å | | | |
| $P^1–O^1$ | 1.459(2) | 1.459(2) | 1.436(3) | 1.458(2) | 1.461(2) | 1.464(2) |
| $P^1–O^2$ | 1.567(2) | 1.571(3) | 1.537(3) | 1.573(2) | 1.564(2) | 1.560(3) |
| $P^1–O^3$ | 1.573(2) | 1.562(3) | 1.563(3) | 1.562(2) | 1.565(2) | 1.561(3) |
| $P^1–C^1$ | 1.811(2) | 1.802(3) | 1.801(3) | 1.806(2) | 1.812(3) | 1.806(3) |
| $N^1–N^2$ | 1.377(3) | 1.383(4) | 1.383(4) | 1.397(3) | 1.415(3) | 1.417(3) |
| $N^1–C^{12(15)}$ | 1.362(3) | 1.360(5) | 1.349(5) | 1.352(3) | 1.355(4) | 1.349(3) |
| $N^2–C^3$ | 1.275(3) | 1.283(5) | 1.280(5) | 1.276(3) | 1.275(3) | 1.269(3) |
| $N^3–O^5$ | 1.228(3) | 1.235(5) | 1.227(5) | – | 1.236(6) | 1.211(5) |
| $N^3–O^6$ | 1.230(3) | 1.230(5) | 1.224(6) | – | 1.229(6) | 1.200(4) |
| $N^3–C^9$ | 1.443(4) | – | 1.460(5) | – | 1.470(4) | 1.475(4) |
| $O^2–C^8$ | 1.414(4) | 1.415(5) | 1.355(6) | 1.422(4) | 1.413(4) | 1.357(4) |
| $O^3–C^7$ | 1.448(3) | 1.390(6) | 1.459(11) | 1.402(4) | 1.425(4) | 1.398(4) |
| $O^4–C^{15}$ | – | – | – | 1.213(3) | 1.221(3) | 1.219(3) |
| $C^1–C^2$ | 1.536(4) | 1.554(4) | 1.544(5) | 1.552(3) | 1.548(4) | 1.555(4) |
| $C^1–C^5$ | 1.529(4) | 1.531(5) | 1.530(5) | 1.530(4) | 1.554(4) | 1.539(4) |
| $C^1–C^6$ | 1.533(4) | 1.544(5) | 1.534(5) | 1.537(4) | 1.535(4) | 1.532(4) |
| $C^2–C^3$ | 1.511(3) | 1.505(5) | 1.502(5) | 1.504(3) | 1.517(3) | 1.509(3) |
| $C^3–C^4$ | 1.496(4) | 1.502(6) | 1.482(6) | 1.498(3) | 1.495(4) | 1.500(4) |
| $C^{12}–C^{15}$ | – | – | – | 1.500(3) | 1.513(4) | 1.514(4) |
| | | | Bond angle, deg | | | |
| $P^1C^1C^5$ | 105.8(2) | 108.7(2) | 107.0(2) | 110.5(2) | 108.7(2) | 110.1(2) |
| $P^1C^1C^6$ | 108.1(2) | 110.3(2) | 108.1(2) | 107.3(2) | 107.2(2) | 107.9(2) |
| $P^1C^1C^2$ | 107.8(2) | 105.8(2) | 109.7(2) | 105.7(2) | 107.7(2) | 106.5(2) |
| $P^1O^2C^8$ | 124.4(2) | 121.3(2) | 127.5(3) | 120.0(2) | 123.9(2) | 128.8(3) |
| $P^1O^3C^7$ | 119.3(2) | 124.6(3) | 119.9(6) | 124.9(2) | 122.5 (2) | 124.4(3) |
| $N^1N^2C^3$ | 117.2(2) | 115.4(3) | 116.9(3) | 115.2(2) | 116.9(2) | 116.6(2) |
| $N^1C^{15}C^{12}$ | – | – | – | 114.5(2) | 115.7(2) | 115.5(2) |
| $N^1C^{15}O^4$ | – | – | – | 123.5(2) | 123.5(2) | 123.6(2) |
| $N^2N^1C^{12(15)}$ | 119.3(2) | 119.3(3) | 119.2(3) | 119.2(2) | 120.5(2) | 121.2(2) |
| $N^2C^3C^4$ | 126.3(2) | 124.8(3) | 125.3(3) | 124.6(2) | 125.4(2) | 126.4(2) |
| $N^2C^3C^2$ | 119.5(2) | 115.2(3) | 115.3(3) | 116.2(2) | 114.2(2) | 114.9(2) |
| $O^1P^1O^3$ | 114.8(1) | 114.1(1) | 121.8(2) | 113.1(1) | 113.3(1) | 113.9(2) |
| $O^1P^1O^2$ | 113.5(1) | 114.2(2) | 115.0(2) | 114.6(1) | 113.1(1) | 114.3(2) |
| $O^2P^1O^3$ | 103.1(1) | 104.3(2) | 85.4(3) | 104.9(1) | 105.6(2) | 103.8(2) |
| $O^4C^{15}C^{12}$ | – | – | – | 122.0(2) | 120.8(3) | 120.9(3) |
| $C^1P^1O^1$ | 115.4(1) | 116.1(1) | 116.2(2) | 115.5(1) | 116.2(1) | 115.8(1) |
| $C^1P^1O^3$ | 103.4(1) | 103.5(2) | 108.9(2) | 105.2(1) | 103.9(1) | 103.9(1) |
| $C^1P^1O^2$ | 105.3(1) | 103.0(1) | 104.5(2) | 102.2(1) | 103.5(1) | 103.8(1) |
| $C^1C^2C^3$ | 120.9(2) | 116.0(3) | 115.3(3) | 115.3(2) | 114.3(2) | 114.1(2) |
| $C^2C^1C^5$ | 112.0(2) | 109.9(2) | 112.1(3) | 111.1(2) | 112.1(3) | 111.6(3) |
| $C^2C^1C^6$ | 112.1(2) | 112.3(3) | 110.5(3) | 112.0(2) | 110.1(2) | 110.6(2) |
| $C^2C^3C^4$ | 114.2(2) | 120.0(3) | 119.5(3) | 119.0(2) | 120.3(2) | 118.7(2) |
| $C^5C^1C^6$ | 110.6(2) | 109.7(3) | 109.4(3) | 110.2(2) | 110.8(3) | 110.1(3) |

**Table 3.** (Contd.)

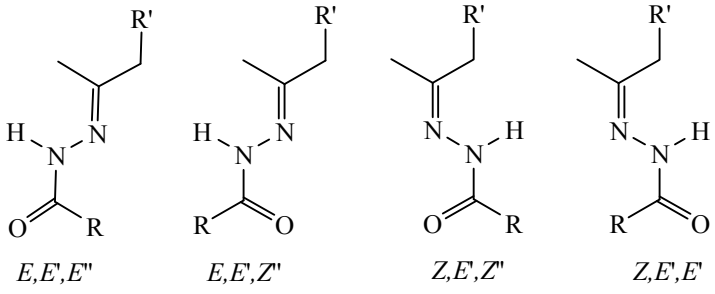
| Parameter | III | IV[a] | V[b] | VI | VIIA | VIIB |
|---|---|---|---|---|---|---|
| | | | Torsion angle, deg | | | |
| $P^1C^1C^2C^3$ | 176.4(2) | 177.4(3) | 179.2(2) | –169.6(2) | 171.7(2) | 175.5(2) |
| $O^1P^1O^2C^8$ | 1.7(3) | –50.4(4) | –16.8(6) | –55.3(3) | 32.7(3) | –24.4(5) |
| $O^3P^1O^2C^8$ | 126.4(3) | 74.9(3) | 106.3(6) | 69.4(3) | –91.8(3) | 100.3(4) |
| $C^1P^1O^2C^8$ | 125.5(3) | –177.2(3) | –145.3(5) | 179.0(2) | 159.3(3) | –151.4(4) |
| $O^1P^1O^3C^7$ | 60.3(2) | 21.0(4) | –39.1(8) | 4.0(3) | –44.3(3) | 30.7(4) |
| $O^2P^1O^3C^7$ | –63.5(2) | –104.3(4) | –155.8(7) | –121.6(3) | 80.0(3) | –94.2(4) |
| $C^1P^1O^3C^7$ | –173.1(2) | 148.2(3) | 100.4(7) | 131.0(3) | –171.3(3) | 157.5(4) |
| $O^1P^1C^1C^2$ | 179.1(2) | 57.7(3) | 170.8(2) | 60.4(2) | –59.5(3) | 61.3(2) |
| $O^1P^1C^1C^5$ | –59.2(2) | –60.4(2) | 49.0(3) | –179.3(2) | 178.9(3) | –177.6(3) |
| $O^1P^1C^1C^6$ | 59.4(2) | 179.3(2) | –68.7(3) | –59.2(2) | 59.0(3) | –57.5(3) |
| $O^2P^1C^1C^2$ | –53.1(2) | –176.7(2) | –61.4(3) | –174.4(1) | 175.9(2) | –172.6(2) |
| $O^2P^1C^1C^5$ | 66.8(2) | 65.3(2) | 176.8(3) | –54.1(2) | 54.3(3) | –51.5(3) |
| $O^2P^1C^1C^6$ | –174.6(2) | –55.1(3) | 59.1(3) | 66.0(2) | –65.6(2) | 68.6(3) |
| $O^3P^1C^1C^2$ | 54.7(2) | –68.2(2) | 28.7(3) | –65.1(2) | 65.7(2) | –64.4(2) |
| $O^3P^1C^1C^5$ | 174.6(2) | 173.7(2) | –93.1(3) | 55.3(2) | –55.9(3) | 56.8(3) |
| $O^3P^1C^1C^6$ | –66.8(2) | 53.4(3) | 149.2(3) | 175.3(2) | –175.9(2) | 176.8(3) |
| $N^1N^2C^3C^2$ | 178.2(2) | 179.6(3) | –179.4(3) | 179.2(2) | 178.1(3) | –177.1(3) |
| $N^1N^2C^3C^4$ | 0.5(4) | 0.9(5) | 0.7(5) | –5.1(3) | –4.1(6) | 6.0(5) |
| $N^1C^{15}C^{12}C^{11}$ | – | – | – | 26.5(3) | –13.4(4) | –4.9(5) |
| $N^1C^{15}C^{12}C^{13}$ | – | – | – | –156.6(2) | 168.7(3) | 174.6(3) |
| $N^2N^1C^{15}C^{12}$ | – | – | – | –178.9(2) | –166.4(2) | 167.2(3) |
| $N^2N^1C^{15}O^4$ | – | – | – | –2.5(3) | 15.0(4) | –13.6(5) |
| $N^2N^1C^{15}C^{12}$ | – | – | – | –179.2(2) | –166.0(2) | 166.9(2) |
| $N^2N^1C^{12}C^{11}$ | 1.6(4) | –177.3(3) | –179.4(3) | – | – | – |
| $N^2N^1C^{12}C^{13}$ | –178.6(2) | 2.6(5) | –0.1(5) | – | – | – |
| $O^4C^{15}C^{12}C^{11}$ | – | – | – | –150.0(2) | 165.2(3) | 175.9(4) |
| $O^4C^{15}C^{12}C^{13}$ | – | – | – | 26.9(3) | –12.6(4) | –4.6(5) |
| $O^5N^3C^9C^{14}$ | 177.1(3) | – | 1.3(6) | – | 169.0(4) | 173.7(4) |
| $O^5N^3C^9C^{10}$ | –2.2(5) | – | –178.4(4) | – | 9.7(5) | –6.5(6) |
| $O^6N^3C^9C^{10}$ | 177.7(3) | – | 1.6(6) | – | 169.9(4) | 173.9(5) |
| $O^6N^3C^9C^{14}$ | –3.0(4) | – | –178.7(4) | – | –11.5(5) | –6.0(6) |
| $O^6N^3C^{11}C^{10}$ | – | –177.7(4) | –178.1(3) | – | – | – |
| $O^6N^3C^{11}C^{12}$ | – | 1.7(6) | 1.3(5) | – | – | – |
| $O^5N^3C^{11}C^{10}$ | – | –1.2(6) | 0.7(4) | – | – | – |
| $O^5N^3C^{11}C^{12}$ | – | 178.2(4) | –179.9(3) | – | – | – |
| $C^1C^2C^3N^2$ | –2.8(4) | 96.1(4) | 78.1(4) | –94.8(2) | –104.2(3) | 86.9(3) |
| $C^1C^2C^3C^4$ | 178.3(3) | –85.1(4) | –102.0(4) | 89.3(3) | 77.9(5) | –95.9(3) |
| $C^3N^2N^1C^{12}$ | 178.9(3) | 176.6(3) | 175.7(3) | – | – | – |
| $C^3N^2N^1C^{15}$ | – | – | – | 158.6(2) | –71.5(4) | 67.9(4) |
| $C^3C^2C^1C^5$ | 60.4(4) | –65.4(4) | –62.1(4) | 70.5(2) | –68.9(3) | 55.3(3) |
| $C^3C^2C^1C^6$ | –64.7(4) | 57.0(4) | 60.1(4) | –53.1(3) | 55.1(3) | –67.6(3) |
| $C^3N^2N^1C^{15}$ | – | – | – | 158.8(2) | –72.1(4) | 68.6(4) |

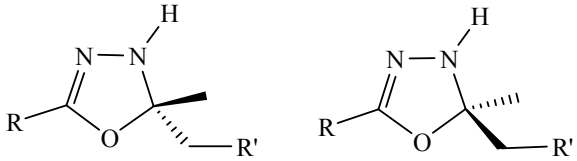
[a] Bond lengths in the disordered fragment given for the maximum population 0.62; $N^4$–$O^7$ 1.223(4) Å, $N^4$–$O^8$ 1.230(4) Å, $N^3$–$C^9$ 1.460(5) Å, $N^4$–$C^{11}$ 1.445(4) Å. [b] $N^3$–$C^{11}$ bond length is 1.438(6) Å.

**Table 4.** Deviations of atoms from the [$N^1N^2C^2C^3C^4$] plane *P*(1) in the molecules of the dimephosphone aryl- and aroylhydrazones **III–VII**

| Parameter | III | IV | V | VI | VIIA | VIIB |
|---|---|---|---|---|---|---|
| The limits of the *P*(1) fragment flatness | 0.010(3) | 0.007(4) | 0.005(3) | 0.021(2) | 0.023(3) | 0.035(3) |
| Deviations of atoms from the *P*(1) plane | | | | | | |
| $C^{15}$ | – | – | – | –0.451(2) | 1.156(4) | –1.150(4) |
| $O^4$ | – | – | – | –0.944(2) | 2.102(3) | –2.081(3) |
| $C^1$ | –0.036(3) | –1.382(3) | –1.369(3) | 1.394(2) | 1.385(3) | –1.427(3) |
| $C^5$ | 1.156(4) | –2.239(4) | –1.893(5) | 2.155(3) | 1.820(5) | –2.380(4) |
| $C^6$ | –1.354(4) | –2.133(4) | –2.402(4) | 2.237(3) | 2.445(5) | –2.017(4) |
| $P^1$ | 0.1116(8) | –1.0465(9) | –1.205(1) | 1.0681(6) | 1.245(1) | –1.207(1) |
| $O^1$ | 0.107(2) | –0.325(2) | –2.341(2) | 0.361(2) | 0.871(3) | –0.362(3) |
| $O^2$ | 1.400(2) | –2.471(3) | –0.757(4) | 2.506(2) | 2.640(3) | –2.666(4) |
| $O^3$ | –1.050(2) | –0.320(3) | 0.255(4) | 0.318(2) | 0.236(3) | –0.686(3) |
| $C^7$ | –1.153(4) | 0.657(5) | 0.54(1) | –0.868(4) | –0.300(5) | 0.038(6) |
| $C^8$ | 2.485(4) | –2.661(4) | –1.085(6) | 2.683(4) | 3.168(6) | –3.135(7) |
| The angle of rotation of the benzene ring relative to the *P*(1) plane | 2.3(2) | 3.1(2) | 3.5(2) | 1.7(1) | 80.0(2) | 60.0(2) |
| The angle of rotation of the nitro group relative to the plane of the benzene ring | 2.5(4) | 3.7(5) | $N^3O^5O^6$ 1.5(5)<br>$N^4O^7O^8$ 2.4(4) | – | 11.1(5) | 6.7(6) |

H-bond between the NH group of the hydrazone fragment and the proton acceptor in the ylidene fragment (in this case, phosphoryl group) can also stabilize the *Z*-isomer relatively to the C=N multiple bond, as has been observed in the case of pyridyl-2-aldehyde aroylhydrazones [20].




**XIIIa** **XIIIb**

R = $CMe_2P(O)(OMe)_2$.

According to IR spectroscopy, both dimephosphone benzoyl- and 4-nitrobenzoylhydrazones **VI, VII** in the crystals exist in one form, and the NH, C=O, and C=N groups give only one absorption band each (Table 1). In solutions, the aroylhydrazones **VI, VII** mostly are in two forms, although one of them dominates. Based on the data of analysis of the structure of dimephosphone arylhydrazones **II–V** and published results [6, 7, 17–20],

**Table 5.** The interaction parameters in the crystals of dimephosphone aryl- and aroylhydrazones **III–VII**

| D–H···A | D–H, Å | H···A, Å | D···A, Å | DHA, deg | Symmetry operations |
|---|---|---|---|---|---|
| | | | **III** | | |
| $N^{1}$–$H^{1}$···$O^{1'}$ | 0.80(3) | 2.20(3) | 2.975(3) | 165(3) | *x*, 1 + *y*, *z* |
| $C^{13}$–$H^{13}$···$O^{1'}$ | 0.93 | 2.50 | 3.280(3) | 141.0 | *x*, 1 + *y*, *z* |
| $C^{2}$–$H^{21}$···$O^{3}$ | 0.97 | 2.55 | 2.984(4) | 107.5 | – |
| $C^{2}$–$H^{22}$···$O^{2}$ | 0.97 | 2.51 | 3.007(4) | 112.0 | – |
| $C^{5}$–$H^{53}$···$N^{2}$ | 0.96 | 2.46 | 3.063(4) | 120.4 | – |
| $C^{6}$–$H^{63}$···$N^{2}$ | 0.96 | 2.62 | 3.183(4) | 117.8 | – |
| | | | **IV** | | |
| $N^{1}$–$H^{1}$···$O^{6}$ | 0.86(3) | 1.98(3) | 2.593(4) | 127(3) | – |
| $N^{1}$–$H^{1}$···$N^{3}$ | 0.86(3) | 2.62(3) | 2.894(5) | 100(2) | – |
| $C^{9}$–$H^{9}$···$O^{1'}$ | 0.93 | 2.52 | 3.401(6) | 159.0 | –*x*, 1 – *y*, 1–*z* |
| $C^{8}$–$H^{82}$···$O^{5''}$ | 0.96 | 2.49 | 3.232(5) | 134.0 | –1+*x*, –1 + *y*, –1 + *z* |
| $C^{10}$–$H^{10}$···$O^{5}$ | 0.93 | 2.35 | 2.674(7) | 100.0 | – |
| $C^{13}$–$H^{13}$···$N^{2}$ | 0.93 | 2.41 | 2.742(5) | 101.0 | – |
| $C^{7}$–$H^{71}$···$O^{1}$ | 0.96 | 2.57 | 2.987(6) | 106.0 | – |
| | | | **V** | | |
| $N^{1}$–$H^{1}$···$O^{8}$ | 0.84(4) | 1.97(4) | 2.611(4) | 132(4) | – |
| $N^{1}$–$H^{1}$···$N^{4}$ | 0.84(4) | 2.58(4) | 2.913(4) | 105(3) | – |
| $C^{14}$–$H^{14}$···$O^{1'}$ | 0.93 | 2.53 | 3.282(5) | 139.0 | 1 – *x*, 1 – *y*, –*z* |
| $C^{6}$–$H^{63}$···$O^{5''}$ | 0.96 | 2.56 | 3.525(5) | 178.0 | –1/2 + *x*, 1/2 – *y*, 1/2 + *z* |
| $C^{13}$–$H^{13}$···$N^{2}$ | 0.93 | 2.40 | 2.731(4) | 101.0 | – |
| $C^{2}$–$H^{21}$···$O^{3}$ | 0.97 | 2.56 | 2.920(5) | 102.0 | – |
| $C^{5}$–$H^{53}$···$N^{2}$ | 0.96 | 2.58 | 3.068(5) | 112.0 | – |
| | | | **VI** | | |
| $N^{1}$–$H^{1}$···$O^{1'}$ | 0.87(3) | 2.06(3) | 2.899(3) | 163(2) | *x*, 1/2 – *y*, –1/2 + *z* |
| $C^{4}$–$H^{42}$···$O^{1'}$ | 0.96 | 2.44 | 3.242(3) | 141.0 | *x*, 1/2 – *y*, –1/2 + *z* |
| $C^{7}$–$H^{72}$···$O^{4''}$ | 0.96 | 2.53 | 3.231(4) | 130.0 | *x*, 3/2 – *y*, 1/2 + *z* |
| $C^{5}$–$H^{51}$···$O^{2}$ | 0.96 | 2.59 | 2.998(4) | 106.0 | – |
| | | | **VII** | | |
| $N^{1A}$–$H^{1A}$···$O^{1B}$ | 0.81(3) | 2.04(3) | 2.841(4) | 170(3) | –1 + *x*, 1 + *y*, *z* |
| $N^{1B}$–$H^{1B}$···$O^{1A}$ | 0.87(3) | 1.99(3) | 2.826(3) | 164(2) | 1 + *x*, –1 + *y*, *z* |
| $C^{10B}$–$H^{10B}$···$O^{5A'}$ | 0.93 | 2.55 | 3.322(6) | 140.6 | *x*, *y*, 1 + *z* |
| $C^{11A}$–$H^{11A}$···$O^{1B}$ | 0.93 | 2.57 | 3.320(5) | 138.3 | –1 + *x*, 1 + *y*, *z* |
| $C^{11B}$–$H^{11B}$···$O^{1A}$ | 0.93 | 2.42 | 3.301(5) | 157.5 | 1 + *x*, –1 + *y*, *z* |
| $C^{2B}$–$H^{21B}$···$N^{2A}$ | 0.97 | 2.56 | 3.518(4) | 168.9 | 1 + *x*, –1 + *y*, *z* |
| $C^{7A}$–$H^{71A}$···$N^{1B''}$ | 0.96 | 2.61 | 3.567(6) | 170.0 | –*x*, 1 – *y*, 1 – *z* |
| $C^{13B}$–$H^{13B}$···$O^{4A}$ | 0.93 | 2.50 | 3.255(5) | 138.1 | – |
| $C^{13B}$–$H^{13B}$···$O^{4B}$ | 0.93 | 2.46 | 2.776(4) | 100.3 | – |
| $C^{4B}$–$H^{41B}$···$O^{4B}$ | 0.96 | 2.52 | 2.954(5) | 107.4 | – |
| $C^{4A}$–$H^{43A}$···$O^{4A}$ | 0.96 | 2.49 | 2.998(6) | 112.7 | – |
| $C^{5B}$–$H^{51B}$···$O^{2B}$ | 0.96 | 2.55 | 2.996(5) | 108.8 | – |
| $C^{5A}$–$H^{53A}$···$O^{2A}$ | 0.96 | 2.53 | 3.005(5) | 110.4 | – |

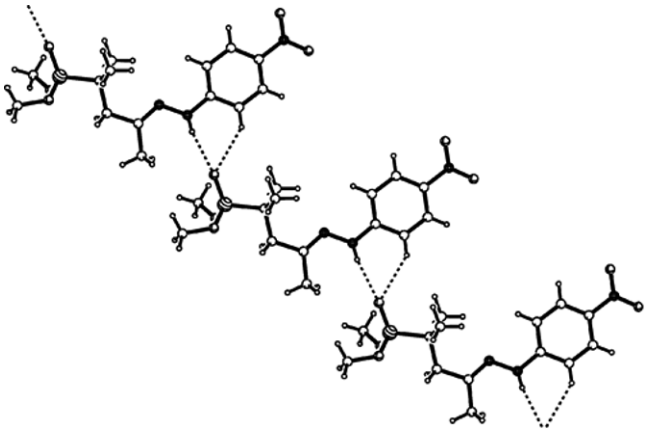


**Fig. 4.** The system of hydrogen bonds in the crystal of dimephosphone 4-nitrophenylhydrazone **III**.

we can conclude that the more stable form in crystals and in solutions is the $E_{C=N}$ isomer. To clarify the conformation of the amide fragment we used the X-ray diffraction analysis. We found that in contrast to arylhydrazones **III–V** and benzoylhydrazone **VI** containing in the unit cell of the crystal only one independent molecule of respective compound, the unit cell of 4-nitrobenzoylhydrazone **VII** includes two independent molecules, **VIIA** and **VIIB** (Figs. 7, 8). Although these molecules are $E_{C=N}$ isomers and the $E_{C(O)–N}$ conformers, overall conformation of the hydrazones and ylidene fragments differ significantly from those observed in the molecules of arylhydrazones **III–V**. Because of the presence of carbonyl group in aroylhydrazones **VI, VII** the interaction of the electronic systems of aryl and hydrazone groups (conjugation) is weaker resulting in a lengthening of the N–N bonds, which in the molecules of 4-nitrobenzoylhydrazones **VIIA** and **VIIB** reach 1.415(3) and 1.417(3) Å, respectively. Despite the fact that isopropylidenehydrazone fragment *P*(2) [$C^2C^3(C^4)=N^2N^1$] in these molecules is also flat, the imine bond and amide fragment are separated, especially under the influence of 4-nitrophenyl substituents. The decrease in the $N^1–N^2$ bond order leads to about 20° turn of the fragments around this bond in the benzoylhydrazone **VI** molecule and approximately to 70° (in the opposite direction) in the molecule of 4-nitrobenzoylhydrazone **VIIA, VIIB**) (see torsion angles in Table 3). In the molecules of **VII** there is also a turn of acyl fragments around the amide bond $C^{15}–N^1$ about 14°, while in the molecule of benzoylhydrazone **VI** it does not exceed 3°. On the other hand, in the molecule **VI** the phenyl rings are much more turned around the amide–aryl bond ($C^{15}–C^{12}$): ~27° against ~13° in the molecule of 4-nitrobenzoylhydrazone **VIIA** and ~5° in molecules of the other independent form **VIIA**. These changes can also be attributed to the influence of the nitro group on the electron density distribution in the acyl moiety. A decrease in the interaction of nitro group in the position 4 of the phenyl ring with hydrazone fragment in the molecule of acylhydrazone **VII** compared with 4-nitrophenylhydrazone **III** appears as an increase in the rotation angle of nitro groups with respect to the phenyl ring. In molecules **VIIA, VIIB** the angles are ~11.5° and ~6°, respectively, while in the molecule of arylhydrazone **III** it does not exceed 3°.

The stereochemistry of the dimethoxyphosphorylbutyl fragment in aroylhydrazone molecules **VI** and **VII** is closer to that of the molecules of 2-nitro- and 2,4-dinitrophenylhydrazones.

Aroylhydrazone **VI** molecules form in the crystals a 1D-supramolecular structure similar to that of arylhydrazone **III,** namely, the chains along the axis 0*z* (Fig. 9). In the crystal of compound **VII** a 0D structure is formed through the classical hydrogen bonds $N^{1A}–H^{1A}\cdots O^{1B}$ and $N^{1B}–H^{1B}\cdots O^{1A}$ (Table. 5), the dimers of molecules **VIIA, VIIB** (Fig. 10). The short contacts of the H···O type in molecule **VI** form layers parallel to the *b*0*c* plane of the crystal, and in the crystal of **VII** similar contacts lead to the formation of three-dimensional structure (Table 5).

The NMR spectra of dimephosphone aryl- and aroylhydrazones **III–VII** in solution of trifluoroacetic acid exhibit some peculiarities. The signals of the second forms of these hydrazones appear almost immediately after the dissolution, and their intensity increases rapidly (Table 2). The signals of methyl groups adjacent to the phosphoryl group are shifted upfield by 0.3–0.5 ppm compared with the spectra of solutions in other solvents. A similar but not so clear effect occurs at the formation of the dimephosphone complexes with calix[4]resorcinol tetramethylsulfonate, which is attributed not only to the entry of a dimephosphone molecule into the calix[4]arene cavity, but also by the intermolecular hydrogen bonding of the phosphoryl oxygen with one of the hydroxyls of the macrocycle [22]. Since the signals of methyl and methylene groups linked to the hydrazone fragment of arylhydrazones **II–V** are not shifted noticeably at dissolving the compound in trifluoroacetic acid (Table 2) due to the possible protonation of nitrogen atoms, the observed effect may be due to the interaction of

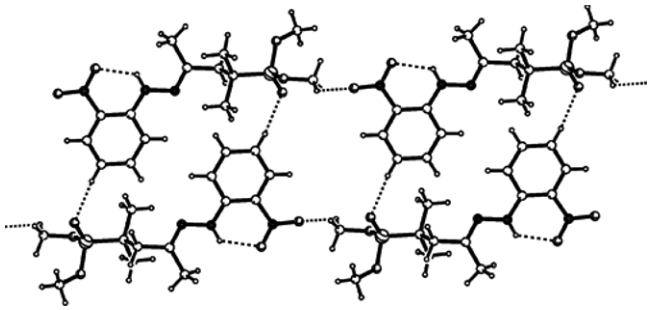


**Fig. 5.** The system of hydrogen bonds in the crystal of dimephosphone 2-nitrophenylhydrazone **IV**.

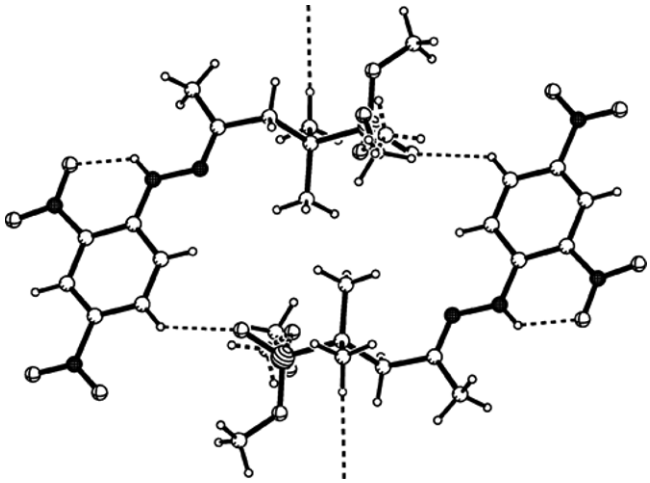


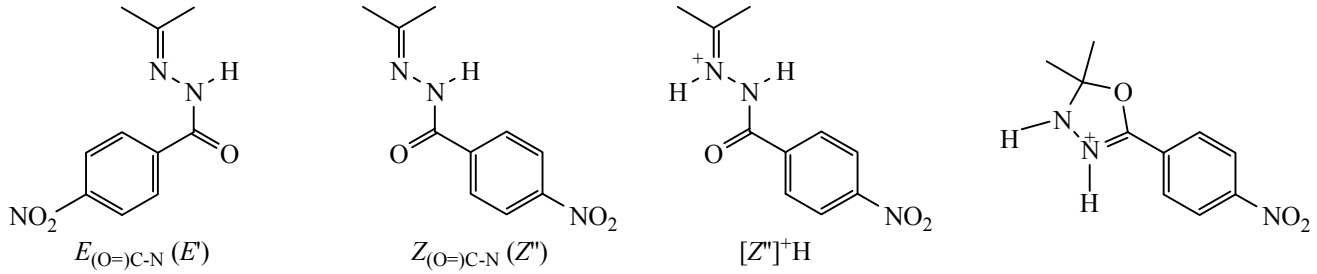
**Fig. 6.** The system of hydrogen bonds in the crystal of dimephosphone 2,4-dinitrophenylhydrazone **V**.

trifluoroacetic acid with the phosphoryl group of hydrazones **II–V**, which consists most probably in the formation of intermolecular $F_3CCOOH\cdots O{=}P$ hydrogen bonds.

In the $^1H$ NMR spectrum of aroylhydrazones **VI, VII** in trifluoroacetic acid the signals of three forms always appear (Table 2). The third form in these spectra is characterized by an upfield shift of not only the signals of the $Me_2C$ fragment but also of the signals of methyl and methylene groups linked to the hydrazone fragment of aroylhydrazones **VI, VII,** which can be due to the change of hybridization of the carbon atom of azomethine group from $sp^2$ in the hydrazones **VI, VII** to $sp^3$ at the formation of a cyclic tautomer **XIIIa** (or **XIIIb**), which seldom but certainly are detected in the acylhydrazones [6, 7, 21]. Most likely, 1,3,4-oxadiazol-2-ine **XIII** can exist in the trifluoroacetic acid solution in a protonated form. Unfortunately, we failed to isolate the cyclic isomers of type **XIII** of acylhydrazones **VI, VII**, or their salts despite numerous attempts. When passing HCl gas into the solutions of a hydrazone in various solvents we isolated most frequently a salt of the corresponding hydrazide and dimephosphone.

A situation similar to the described for dimephosphone aroylhydrazone **VII** is observed in the case of related model compound, acetone 4-nitrobenzoylhydrazone **XIV** (Table 6). According to the IR spectra, the crystals of this compound contain only one amide conformer: there are single absorption peaks due to the stretching vibrations of groups NH, C=O, and C=N at 3261, 1654, and 1634 $cm^{-1}$, respectively. The rate of appearance of the second conformer in solution depends on the nature of the solvent. According to [18], in polar solvents dominates the more polar $E_{N-N}Z_{(O=)C-N}$ conformer (the *Z*" conformer) (Table 6). In $CDCl_3$ and in less polar $CD_3CN$ the $E_{N-N}$, $E_{(O=)C-N}$ conformer (*E*" conformer) appears together with the more polar one just in the process of preparation of the solutions. In a more polar solvent DMSO-$d_6$ the less polar $E_{N-N}$, $E_{(O=)C-N}$ conformer (*E*" conformer) appears only in several days after the dissolution.

In trifluoroacetic acid solution of acetone 4-nitrobenzoylhydrazone **XIV** only two forms are found. One of them we regard as the protonated form of *Z*" conformer, and we suggest that the other is the protonated form of the cyclic tautomer.



$E_{(O=)C\text{-}N}$ (*E*') $Z_{(O=)C\text{-}N}$ (*Z*") $[Z"]^+H$

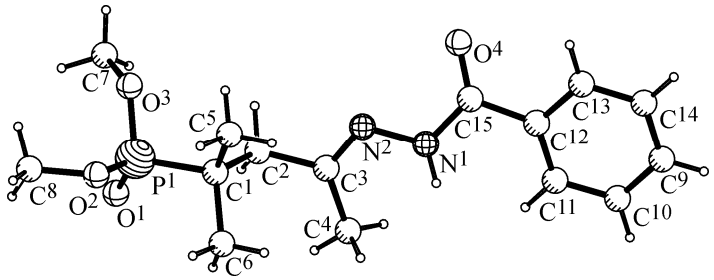



**Fig. 7.** Molecular geometry and numbering of atoms in the crystal of dimephosphone benzoylhydrazone **VI**.

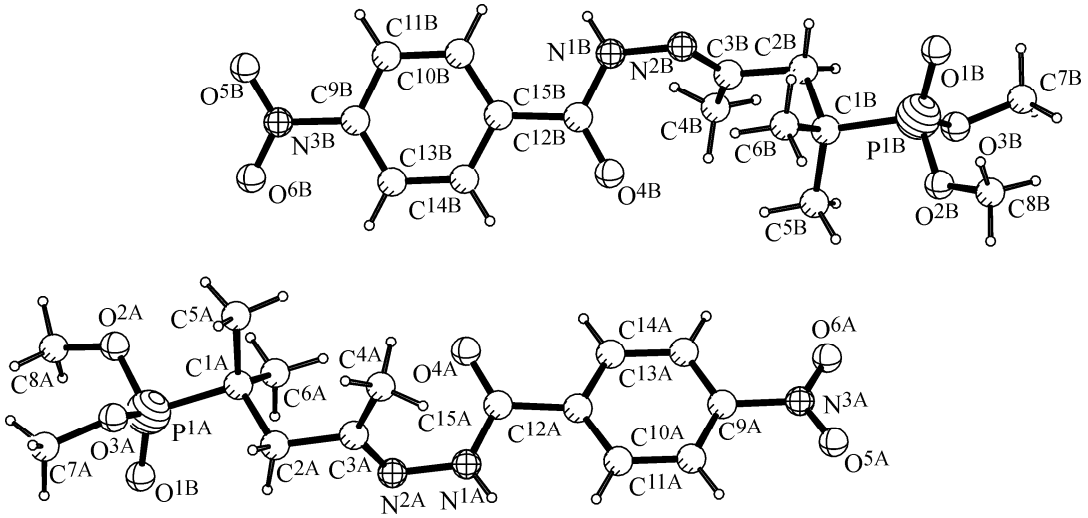



**Fig. 8.** The geometry of the independent molecules and the numbering of atoms in a crystal of dimephosphone 4-nitrobenzoylhydrazone **VII**.

## EXPERIMENTAL

$^1$H and $^{31}$P–{$^1$H} NMR spectra were recorded on a Bruker Avance 600 instrument (600 MHz, $^1$H), and a Bruker Avance-400 (400 MHz, $^1$H, 162 MHz, $^{31}$P) spectrometer, solvent $CDCl_3$, relative to the signal of the solvent, and relative to the external $H_3PO_4$. The spectra of solutions in trifluoroacetic acid were recorded relative to an external reference, acetone-$d_6$. IR spectra were obtained on a Bruker Vector-22 instrument from suspensions of substances in mineral oil or from the KBr pills. The melting points were determined on the Boetius heating block.

**X-ray analysis of the crystals of hydrazones III–VII** was performed on an automatic diffractometer Bruker Smart APEX II CCD: graphite monochromator; λMo$K_\alpha$ = 0.71073 Å; ω-scanning, temperature 293 K. The semiempirical accounting for extinction was carried out using SADABS software [23]. The structure was solved by the direct method with SIR program [24] and refined initially in isotropic, then in anisotropic approximation with the SHELXL-97 software [25]. The hydrogen atoms in structures **III–VII** were placed in geometrically calculated positions and included in the refinement in the *rider* model. All calculations were performed using the WinGX [26] and APEX2 [27] softwares. All figures and analysis of molecular interactions were made with the PLATON software [28]. The study of single crystals of compounds **III–VII** was carried out in the Federal Spectroanalytic Center for Collective Use of the Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of Russian Academy of Sciences on the basis of the Laboratory of Diffraction Methods. Table 7 lists crystallographic parameters and details of the structure refinement of compounds **III–VII**, selected geometric parameters of these molecules are given in Table 3.

**Dimethyl (2-methyl-4-oxopent-2-yl)phosphonate phenylhydrazone (dimephosphone phenylhydrazone) II**. A mixture of 15 g (0.072 mol) of dimethyl (2-methyl-4-oxopent-2-yl)phosphonate (dimephosphone), 10.5 g (0.072 mol) of phenylhydrazine hydrochloride, and 50 ml of methanol was stirred until homogeneous

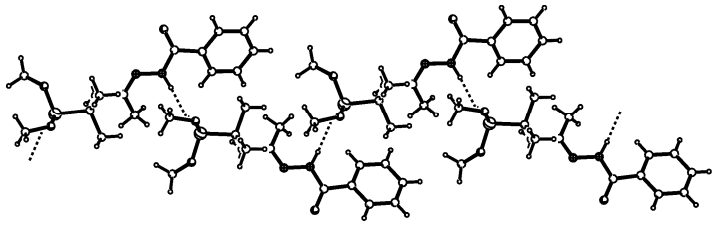


**Fig. 9.** The system of hydrogen bonds in the crystal of dimephosphone benzoylhydrazone **VI**.

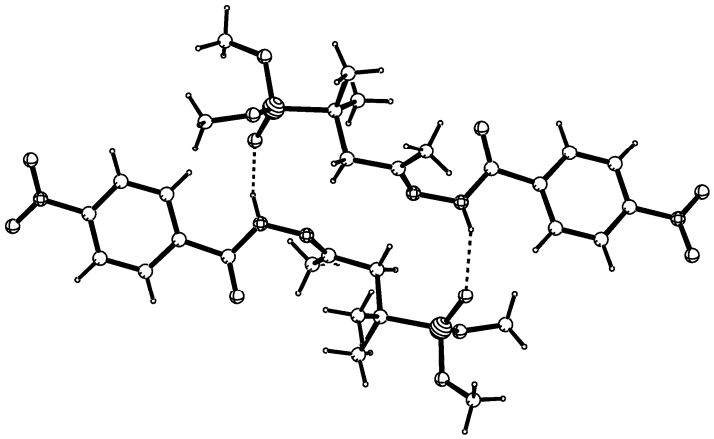


**Fig. 10.** The system of hydrogen bonds in the crystal of dimephosphone 4-nitrobenzoylhydrazone **VII**.

solution formed. After stirring, a drop of conc. $H_2SO_4$ was added and the solution was refluxed for 2 h, then a half of methanol was removed in a vacuum. The residue was dissolved in 150 ml of water, the solution was neutralized to pH 7.0 with saturated solution of $K_2CO_3$. The precipitate was filtered off, washed on the filter with distilled water (5×25 ml), and dried in air to constant weight. Dimephosphone phenylhydrazone, 13.2 g (61%), was isolated as a light beige crystalline powder (Tables 1 and 2).

**Dimephosphone arylhydrazones III–V and aroylhydrazones VI, VII**. A mixture of 1.0 g (0.0048 mol) of dimethyl (2-methyl-4-oxopent-2-yl)phosphonate (dimephosphone) and 0.0048 mol of the corresponding arylhydrazine or arylhydrazide in 20 ml of anhydrous methanol was stirred, and to the solution formed was added a drop of conc. $H_2SO_4$. The resulting mixture was heated under reflux for 1 h, then cooled to room temperature. The precipitated crystals were filtered off immediately or after removal of most part of solvent,

**Table 6.** $^1$H NMR spectral data of the acetone 4-nitrobenzoylhydrazone **XIV**

| Solvent | Form[a] | Ratio of the forms | *Z*-Me | *E*-Me | $H_A$ | $H_B$ | $^3J$, Hz | NH |
|---|---|---|---|---|---|---|---|---|
| | | | | | δ, d | | | |
| $CDCl_3$ | *Z*" | 1.0 | 2.25 | 2.12 | 8.28 | 8.03 | 8.72 | 9.97 |
| | *E*" | 0.2 | 2.16 | 1.99[c] | –[b] | –[b] | –[b] | 9.33 |
| $CD_3CN$ | *Z*" | 1.0 | 2.09 | –[b] | 8.25 | 7.97 | 8.24 | 9.26 |
| | *E*" | 0.5 | –[b] | –[a] | –[b] | –[b] | –[b] | 8.98 |
| DMSO-$d_6$ | *Z*"[c] | | 2.02 | 1.96 | 8.30 | 8.05 | 8.10 | 10.74 |
| Trifluoroacetic acid | *Z*" + $H^+$ | 4.0 | 2.24 | 2.17 | 7.82 | 7.58 | 8.55 | –[d] |
| | Cyclic | 1.0 | 1.76 | | – | 7.53 | 8.88 | –[d] |

[a] *Z*" = $E_{C=N}$, $E_{N–N}$, $Z_{(O=)C–N}$ conformer, *E*" = $E_{C=N}$, $E_{N–N}$, $E_{(O=)C–N}$ conformer. [b] Overlap of signals. [c] In a week the signals of *E*" conformer appear, e.g., at 2.11 ppm and others. [d] Not recorded due to exchange processes.

**Table 7.** Crystallographic parameters and refinement details of the structure of dimephosphone aryl- and aroylhydrazones **III–VII**

| Parameter | **III** | **IV** | **V** | **VI** | **VII** |
|---|---|---|---|---|---|
| Color, habitus | Colorless prismatic | Yellowish needle | Yellowish prismatic | Colorless prismatic | Colorless prismatic |
| Empirical formula | $C_{14}H_{22}N_3O_5P$ | $C_{14}H_{22}N_3O_5P$ | $C_{14}H_{21}N_4O_7P$ | $C_{15}H_{23}N_2O_4P$ | $C_{15}H_{22}N_3O_6P$ |
| Crystal system | Triclinic | Triclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | *P*-1 | *P*-1 | $P2_1/n$ | $P2_1/c$ | *P*-1 |
| The unit cell parameters | *a* 7.135(1),<br>*b* 9.521(2),<br>*c* 12.739(3) Å,<br>α 94.593(2)<br>β 95.951(2)<br>γ 95.230(2)° | *a* 6.319(2),<br>*b* 10.202(2),<br>*c* 14.493(3) Å,<br>α 101.575(2)<br>β 101.383(3)<br>γ 104.449(2)° | *a* 10.191(3),<br>*b* 8.490(3),<br>*c* 21.581(7) Å<br>β 96.246(4)° | *a* 10.778(2),<br>*b* 10.514(2),<br>*c* 14.933(3) Å<br>β 91.306(2)° | *a* 12.629(6),<br>*b* 13.078(6),<br>*c* 13.985(7) Å,<br>α 74.347(5)<br>β 64.859(5)<br>γ 62.023(5)° |
| Volume, $Å^3$ | 853.5(3) | 855.7(3) | 1856(1) | 1691.7(5) | 1841(2) |
| *Z* | 2 | 2 | 4 | 4 | 4 |
| Molecular weight | 343.32 | 343.32 | 388.32 | 326.32 | 371.33 |
| $d_{calc}$, g $cm^{-3}$ | 1.336 | 1.332 | 1.389 | 1.281 | 1.341 |
| Extinction coefficient, μMo, $cm^{-1}$ | 1.89 | 1.88 | 1.92 | 1.81 | 1.85 |
| *F*(000) | 364 | 364 | 816 | 696 | 784 |
| Interval θ | 2.16° ≤ θ ≤ 27.00° | 2.14° ≤ θ ≤ 26.00° | 2.31° ≤ θ ≤ 26.00° | 2.37° ≤ θ ≤ 27.00° | 1.95° ≤ θ ≤ 27.00° |
| $R_{int}$ | 0.0457 | 0.0450 | 0.0535 | 0.0353 | 0.0497 |
| Range of measured indices | $-9 \le h \le 9$,<br>$-11 \le k \le 12$,<br>$-16 \le l \le 16$ | $-7 \le h \le 7$,<br>$-12 \le k \le 12$,<br>$-17 \le l \le 17$ | $-12 \le h \le 12$,<br>$-10 \le k \le 10$,<br>$-26 \le l \le 26$ | $-13 \le h \le 13$,<br>$-13 \le k \le 13$,<br>$-19 \le l \le 19$ | $-16 \le h \le 16$,<br>$-16 \le k \le 16$,<br>$-17 \le l \le 17$ |
| Measured/independent reflections | 9344 / 3686 | 6546 / 3312 | 13634 / 3654 | 13424 / 3693 | 30058 / 8009 |
| Reflections with $I > 2\sigma(I)$ | 2320 | 1788 | 1930 | 2702 | 5291 |
| Final divergence factors | *R* 0.0602,<br>$R_w$ 0.1520<br>$R_{all}$ 0.0975<br>$R_{w\,all}$ 0.1743 | *R* 0.0643,<br>$R_w$ 0.1498<br>$R_{all}$ 0.1179<br>$R_{w\,all}$ 0.1787 | *R* 0.0619,<br>$R_w$ 0.1641<br>$R_{all}$ 0.1172<br>$R_{w\,all}$ 0.1946 | *R* = 0.0542<br>$R_w$ 0.1419<br>$R_{all}$ 0.0743<br>$R_{w\,all}$ 0.1566 | *R* 0.0589,<br>$R_w$ 0.1681<br>$R_{all}$ 0.0889<br>$R_{w\,all}$ 0.1965 |
| Fit parameter | 1.044 | 1.017 | 1.027 | 1.022 | 0.958 |
| Number of refined parameters | 211 | 217 | 258 | 200 | 457 |

sometimes after a short keeping the syrupy mass formed at room temperature. After washing with a small amount of methanol, the product was dried in air. Table 1 lists yields, selected IR spectral data, and elemental analyses, Table 2 contains the data of $^1H$ and $^{31}P$ NMR spectra.

**Acetone 4-nitrobenzoylhydrazone VIII** was prepared from 4-nitrobenzhydrazide and acetone, a slightly yellowish crystalline powder, mp 165°C (from aqueous ethanol), published: 165°C [29]. IR spectrum, $cm^{-1}$: 3251, 3105, 3075, 3039 1654, 1636, 1598, 1524, 1490, 1422, 1349, 1329, 1322, 1303, 1267, 1186, 1142, 1113, 1106, 1076, 1032, 1017, 997, 941. $^1H$ NMR spectra in different solvents are given in Table 6.

## ACKNOWLEDGMENTS

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