Russian Journal of General Chemistry, Vol. 73, No. 5, 2003, pp. 776–781. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 5, 2003, pp. 821–826.

Crystal and Molecular Structure of Acylalmino Derivatives of 1-(2,4,6-Trichlorophenyl)-4,5-dihydropyrazol-5-one

O. N. Kataeva, I. A. Litvinov, D. B. Krivolapov, O. A. Lodochnikova, Sh. H. Abdel-Hafez, A. I. Movchan, and G. A. Chmutova

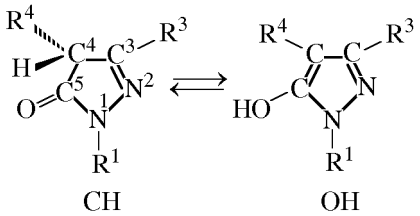
Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

Kazan State University, Kazan, Tatarstan, Russia

Received April 24, 2001

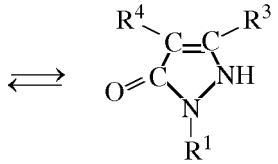
Abstract — The structure of acylamino derivatives of 1-(2,4,6-trichlorophenyl)-4,5-dihydropyrazol-5-one was studied by X-ray diffraction. 3-Acetylamino-1- (2,4,6-trichlorophenyl)-4,5-dihydropyrazol-5-one and 3-benzoylamino-1-(2,4,6-trichlorophenyl)-4,5-dihydropyrazol-5-one exist in crystal as CH tautomers. The nature and number of acylamino groups were found to affect the nature of intermolecular hydrogen bonds in the crystals studied.

Pyrazol-5-ones are widely used in medicine, color photography, analytical chemistry, and agriculture, which is largely due to structural features of these compounds, specifically, their tendency for tautomeric transformations [1–4]. 1-Substituted derivatives can exist in at least three tautomeric forms (CH, OH, and NH).



CH

OH



NH

Moreover, the tautomerism involving substituents R^3 and R^4 is possible. The abundant evidence shows that the state of the tautometic equilibrium of pyrazol-5-ones in solutions strongly depends on the nature of substituents and the medium [5–12].

As judged from the crystal structures available in the Cambridge Structural Database [9–16], the preferred forms of pirazol-5-ones in crystal are those stabilized by intra- and intermolecular H bonding.

In this connection we considered it of interest to study the structure of 3-acetylamino-1-(2,4,6-trichlorophenyl)-4,5-dihydropyrazol-5-one (**Ia**, R^1 = 2,4,6-$Cl_3C_6H_2$, R^3 = Ac, R^4 = H) and 3-benzoylamino-1-(2,4,6-trichlorophenyl)-4,5-dihydropyrazol-5-one (**Ib**, R^1 = 2,4,6-$Cl_3C_6H_2$, R^3 = NHCOPh, R^4 = H). The amide group in compounds **Ia** and **Ib** can stabilize any tautometic form via intermolecular interactions, acting both as proton donor and as proton acceptor. Being in the 3 position of the pyrazolone system, this substituent is also capable of stabilizing the NH form via intramolecular H-complex formation. Our recent studies [17] actually revealed a high lability of the tautomeric equilibria in compounds **Ia** and **Ib** in solvents of different nature.

The samples subjected to X-ray diffraction analysis were synthesized by known procedures [18] and purified by recrystallization from dioxane. Principal parameters of their crystal and molecular structure are presented in the table and Figs. 1–3.

It is readily seen that the structures of these compounds have both common and distinguishing features. In both cases, the CH form is realized, but in compound **Ia** it is stabilized by intermolecular H bonds involving the substituent only, whereas intermolecular bonds in compound **Ib** involve both the substituent NH fragment and the carbonyl oxygen of the pyrazolone system itself. In both cases, "open-chain" infinite structures are formed. It is interesting to note that compounds **Ia** and **Ib** are rare examples of pyrazolone systems in which the CH form is the most stable in the crystal state. A possible reason for this phenomenon is, along with packing effects (stabiliza-

1070-3632/03/7305-0776 $25.00 © 2003 MAIK "Nauka/Interperiodica"

Principal geometric parameters of compounds **Ia, Ib**, and **II** as given by X-ray diffraction analysis

Parameter	Ia	Ib	II	Parameter	Ia	Ib	II
Bond length		*d*, Å		Bond length		*d*, Å	
N^1–N^2	1.413(3)	1.422(3)	1.377(3)	C^4–C^5	1.517(3)	1.509(4)	1.359(3)
N^1–C^5	1.370(3)	1.353(3)	1.352(3)	C^5–O^5/O^{20}	1.205(3)	1.214(3)	1.366(3)
N^2–C^3	1.278(3)	1.279(3)	1.329(3)	N^1–C^6	1.414(3)	1.411(3)	1.420(3)
C^3–C^4	1.485(3)	1.400(3)	1.401(3)	C^3–N^{12}	1.388(3)	1.377(3)	1.383(3)
Bond angle		ω, deg		Bond angle		ω, deg	
$N^2N^1C^5$	113.9(2)	114.3(2)	110.7(2)	$C^4C^5O^5$/O^{20}	130.6(2)	129.6(2)	136.2(2)
$N^1N^2C^3$	105.8(2)	105.3(2)	103.9(2)	$N^1C^5O^5$/O^{20}	124.9(2)	125.9(3)	115.0(2)
$N^2C^3C^4$	114.7(2)	114.4(2)	112.7(2)	$N^2N^1C^6$	118.6(2)	118.9(2)	117.4(2)
$C^3C^4C^5$	101.0(2)	101.5(2)	103.9(2)	$C^5N^1C^6$	127.2(2)	126.7(2)	131.3(2)
$C^4C^5N^1$	104.4(2)	104.5(2)	108.7(2)				
Torsion angle		τ, deg		Torsion angle		τ, deg	
$C^{13}N^{12}C^3N^2$	179.1(2)	179.9(3)	–172.4(2)	$C^6N^1C^5O^5$/O^{20}	3.7(4)	3.4(4)	7.4(3)
$N^2N^1C^6C^7$	–88.4(3)	–95.3(3)	107.7(2)				

tion by intermolecular H bonding), the donor nature of the 3-acylamino substituents.

One more type of intermolecular H bonding, dissimilar to the above two, we revealed in examining the crystal structure of 3-benzoylamino-5-benzoyloxy-1-(2,4,6-trichlorophenyl)pyrazole [**II**, R^1 = 2,4,6-$Cl_3 \cdot C_6H_2$, R^3 = NHCOPh, R^4 = OC(O)Ph]. Compounds of this type are usually formed as by-products in acylation of 3-amino-1-arylpyrazol-5-ones [19].

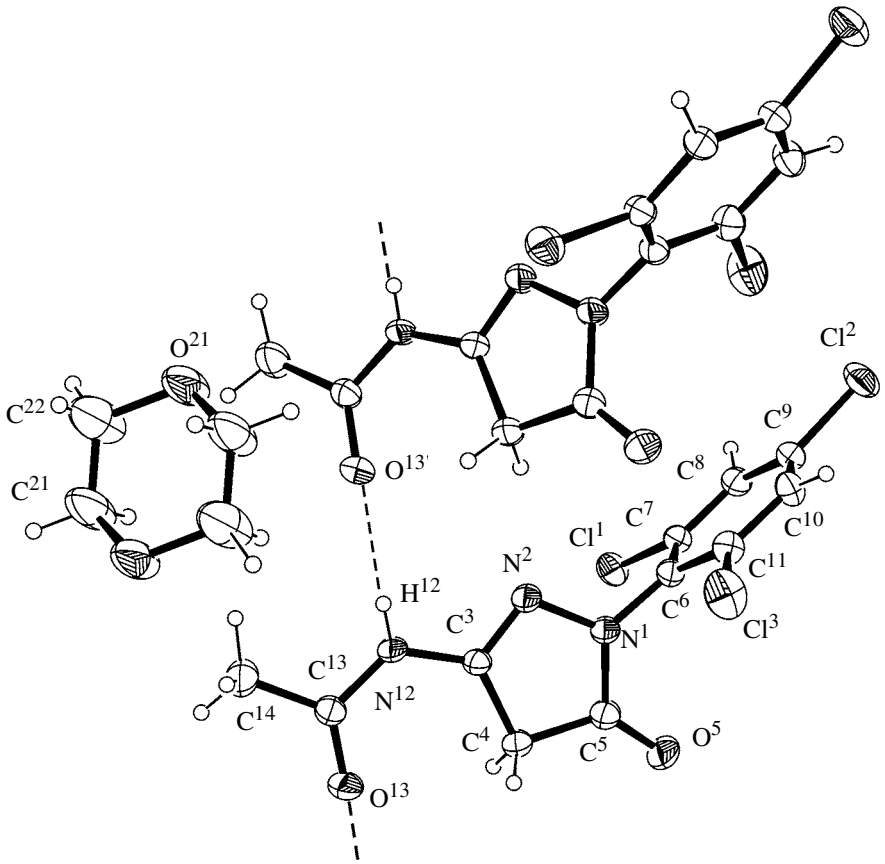


Fig. 1. Numbering of atoms and scheme of H bonds in 3-acetylamino-1-(2,4,6-trichlorophenyl)-4,5-dihydropyrazol-5-one (**Ia**).

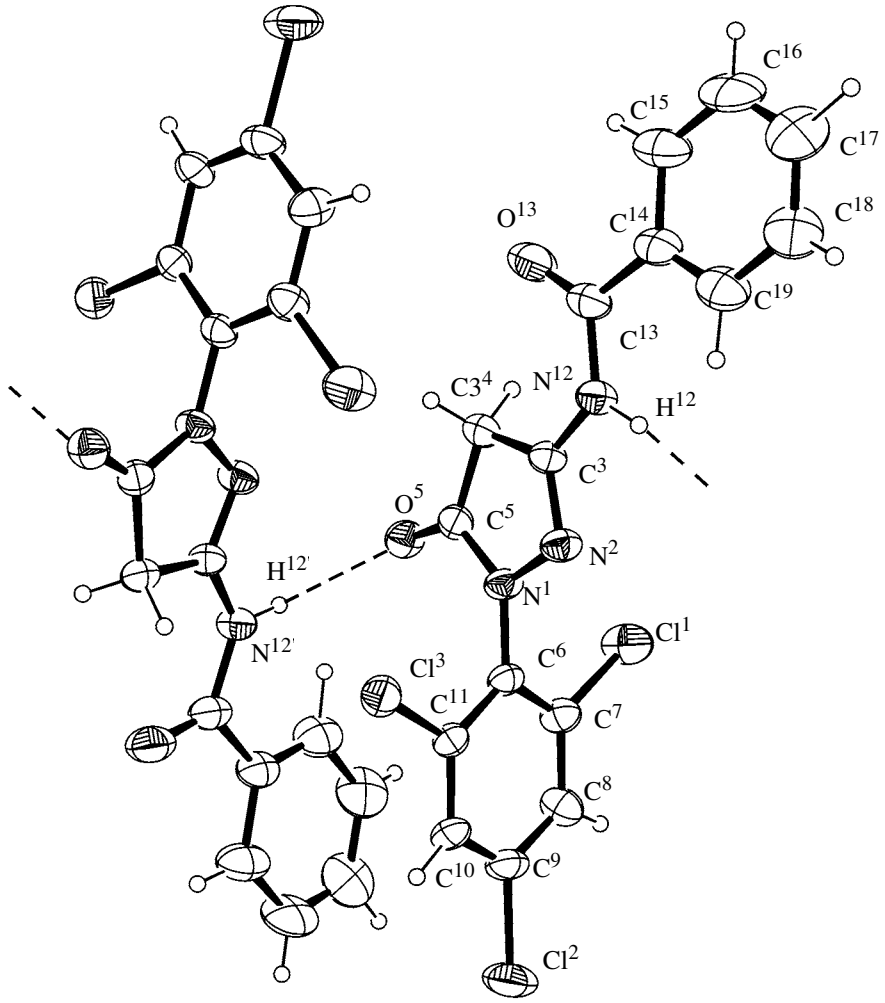


Fig. 2. Numbering of atoms and scheme of H bonds in 3-benzoylamino-1-(2,4,6-trichlorophenyl)-4,5-dihydropyrazol-5-one (**Ib**).

However, the sample in hand was obtained by benzoylation of compound **Ia** under conditions when 3-alkyl-1-arylpyrazol-5-ones give 4-acyl derivatives [2]. In this case, there is no question as to the preferred tautomeric form, since compound **II** has a so-called "fixed" enol form and present as cyclic dimers (Fig. 3) formed by two pairs of H bonds between the substituent NH fragment of one molecule and the pyrazolone N^2 atom of the other.

Hydrogen bonds in compounds **Ia**, **Ib**, and **II** have the following parameters: **Ia**: N^{12}–$H^{12}\cdots O^{13'}$ (1/2 + *x*, 1/2 – *y*, *z*), N^{12}–H^{12} 0.74(3), $H^{12}\cdots O^{13'}$ 2.20(3), $N^{12}\cdots O^{13'}$ 2.929(3), $\angle N^{12}$–$H^{12}\cdots O^{13'}$ 171(3)°; **Ib**: $N^{12'}$–$H^{12'}\cdots O^5$ (1 – *x*, –1/2 + *y*, 1/2 – *z*), $N^{12'}$–$H^{12'}$ 0.815(18), $H^{12'}\cdots O^5$ 2.177(18), $N^{12'}\cdots O^5$ 2.960(2) Å, $\angle N^{12'}$–$H^{12'}\cdots O^5$ 161.0(18)°; and **II**: N^{12}–$H^{12}\cdots N^{2'}$ (3/2 – *x*, *y*, –*z*), N^{12}–H^{12} 0.89(2), $H^{12}\cdots N^{2'}$ 2.18(2), $N^{12}\cdots N^{2'}$ 3.000(2) Å, $\angle N^{12}$–$H^{12}\cdots N^{2'}$ 152(2)°.

Concerning the molecular structure of compounds **Ia**, **Ib**, and **II** we would like to note the following. The amide fragment is almost coplanar to the pyrazolone ring plane in all the three systems (see table) and has the N–H and C=O bonds *s-trans*(*anti*) to the central N–C bond. This configuration is consistent with the conformational effects in other amides, observed experimentally in the crystal and gas phases [20,21], as well as with MNDO and PM3 semiempirical calculations for these and model compounds [17, 22]. According to the calculations, the *s-cis*(*syn*) conformers are less stable by 6–8 kJ/mol. The amide nitrogen atom of the substituent has a nearly planar trigonal configuration (the sum of N^{12} bond angles is 359.5, 358.4, and 358.5° in compounds **Ia**, **Ib**, and **II**, respectively). The length of the central amide bond in all the three compounds is a normal value (1.35–1.38 Å [20,21]) and equals 1.361(3), 1.366(4), and 1.366(4) Å in compounds **Ia**, **Ib**, and **II**, respectively. The ring carbonyl group involved in H bonding

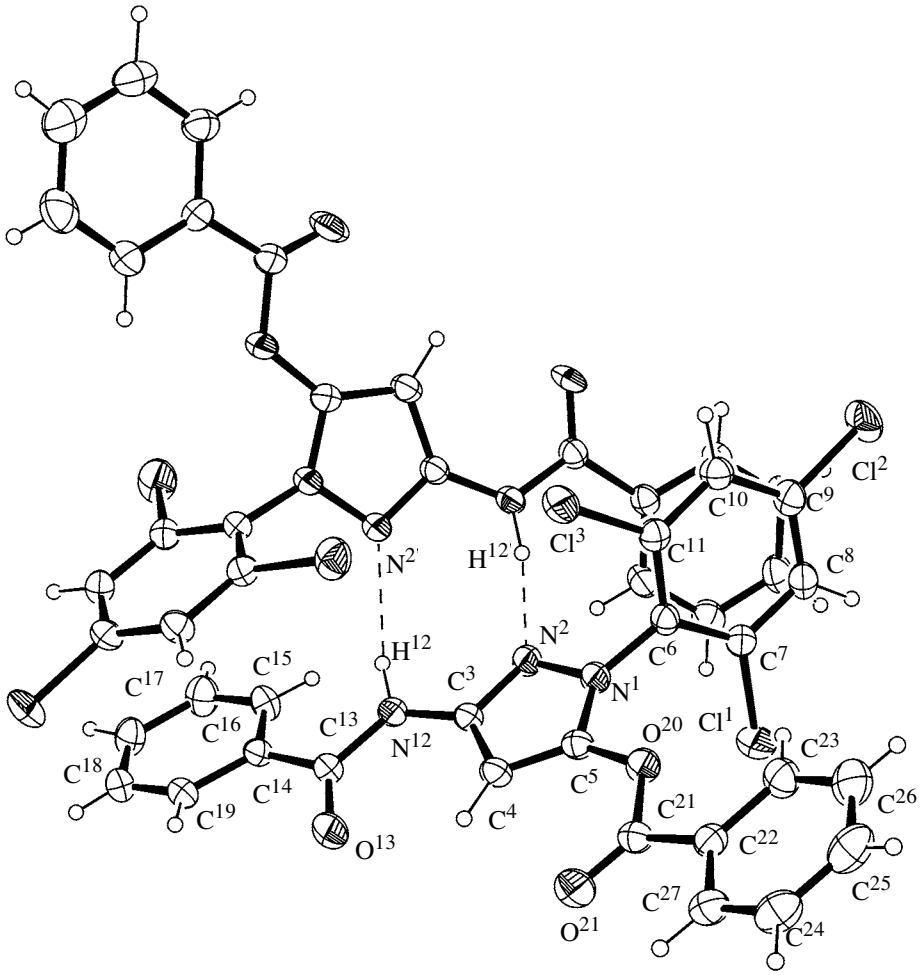


Fig. 3. Numbering of atoms and scheme of H bonds in 3-benzoylamino-5-benzoyloxy-1-(2,4,6-trichlorophenyl)pyrazole (**II**).

is longer than free carbonyl [$d_{C=O}$ 1.214(3) Å in compound **Ib** and 1.205(3) Å in compound **Ia**]. The C=O bond in the amide substituent has almost equally long in all the compounds (within experimental error) or slightly longer in compound **Ia** [1.217(3) Å], where this group is involved in H bonding, compared with compounds **Ib** and **II** [1.213(3) Å], where it is free.

The plane of the trichlorophenyl substituent is almost orthogonal to the plane of the pyrazolone ring in all the three compounds; the benzoyloxy substituent in compound **II** is almost coplanar to the pyrazolone ring (see table).

EXPERIMENTAL

Thin-layer chromatography was performed on Silufol UV-254 plates (development in iodine vapor and fixation with water). Eluent acetone–toluene (1 : 6, by volume).

The IR spectra were measured on a Specord M-80 instrument at 600–4000 cm^{-1} for suspensions in Nujol and 0.1 M solutions (cell thickness d 0.1–0.12 mm). The measurement accuracy was ±1 cm^{-1}.

The ^1H NMR spectra were obtained on a Unity-300 instrument at 25°C, operating frequency 300 MHz. The chemical shifts were determined relative to residual proton signals of deuterochloroform.

X-ray diffraction analysis of compounds **I** and **II** was performed on an Enraf–Nonius CAD-4 diffractometer at 20°C (CuK_α radiation, λ 1.54184 Å).

Crystals of compound **Ia**, $C_{11}H_8N_3O_2Cl_3$, monoclinic. At 20°C: a 9.937(5), b 13.940(7), c 11.339(4) Å; β 95.23(4)°, V 1564(1) $Å^3$, Z 4, d_{calc} 1.552, space group $P2_1/a$.

Crystals of compound **Ib**, $C_{16}H_{10}O_2N_3Cl_3$, monoclinic. At 20°C: a 13.20(1), b 9.40(1)(4), c 14.60(1) Å;

β 110.76(6)°, *V* 1692(3), d_{calc} 1.502, *Z* 4, space group $P2_1/c$.

Crystals of compound **II**, $C_{23}H_{14}O_3Cl_3N_3$, monoclinic. At 20°C: *a* 12.203(6), *b* 12.567(4), *c* 28.045(5); β 94.74(3)°, *V* 4286(3) Å^3, d_{calc} 1.509, *Z* 8, space group *I*2/*a*.

The unit cell parameters and the intensities of 3524 (**Ia**), 2427 (**Ib**), and 5891 (**II**) reflections, 2794 (**Ia**), 1891 (**Ib**), and 2586 (**II**) of which had $I > 3\sigma(I)$, were measured by ω/2θ scanning with variable scanning rate, 16.4 deg/min in θ. No intensity decay of control reflections was observed during measurements. Empirical absorption corrections were applied (μCu 55.662, 51.349, and 42.201 cm^{-1} for structures **Ia**, **Ib**, and **II**, respectively).

The structures were solved by the direct method using the SIR program [23] and refined first isotropically and then anisotropically. Hydrogen atoms were refined isotropically. The final divergence factors were as follows: structure **Ia**: *R* 0.047 and R_W 0.061, on 2607 unique reflections with $F^2 \geq 3\sigma$; structure **Ib**: *R* 0.034 and R_W 0.043, on 1676 unique reflections with $F^2 \geq 3\sigma$; and structure **II**: *R* 0.039 and R_W 0.053, on 2384 unique reflections with $F^2 \geq 3\sigma$. All calculations were performed using the MolEN programs [24] on Alpha Station 200. The molecular drawings were obtained and intermolecular contacts, including hydrogen bonds in crystals, were analyzed using the PLATON program [25]. The crystal data (except for structure factors) obtained in the present work were deposited in the Cambridge Structural Database (supplementary publication CCDC 161446, 161447, 161448).

3-Acetylamino-1-(2,4,6-trichlorophenyl)-4,5-dihydropyrazol-5-one (Ia) was repeatedly recrystallized from dioxane, mp 236–238°C, R_f 0.63. IR spectrum, ν, cm^{-1}: 3250, 3220, 3100 (N–H), 1730 (heteroring C=O), 1680 sh (substituent C=O), 1620 (C=N), 1600, 1570, 1555 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 2.17 s (3H, CH_3), 4.04 s (2H, 4-CH_2), 7.45 s (2H, arom), 8.05 s (1N, 3-NH). Found, %: C 41.64; H 2.39; N 12.99. $C_{11}H_8Cl_3N_3O_2$. Calculated, %: C 41.18; H 2.49; N 13.10.

3-Benzoylamino-1-(2,4,6-trichlorophenyl)-4,5-dihydropyrazol-5-one (Ib), was thrice recrystallized from dioxane, mp 280°C (the unit cell contain one solvate dioxane molecule which is in a special position in the symmetry center), R_f 0.46. IR spectrum, ν, cm^{-1}: 3160, 3090 (N–H), 1700 (heteroring C=O), 1680 sh [C=O, NHC(O)Ph], 1620 (C=N), 1580, 1560, 1518 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 4.22 s (2H, 4-CH_2), 7.44–7.87 m (7H, arom), 8.61 s (1H, 3-NH). Found, %: C 50.20; H 2.61; Cl 27.80. $C_{16}H_{10} \cdot Cl_3N_3O_2$. Calculated, %: C 50.18; H 2.69; Cl 27.60.

3-Benzoylamino-5-benzoyloxy-1-(2,4,6-trichlorophenyl)pyrazole (II). A mixture of 2.6 mmol of a finely ground compound **Ib** and 30 ml of 1,4-dioxane was heated to 50°C. Calcium hydroxide, 0.386 g, was added with vigorous stirring and then, dropwise, over the course of 1 min, 0.367 g of a freshly distilled benzoyl chloride (heat release was observed). The reaction mixture was refluxed for 30 min, cooled, and poured into a mixture of 2.28 ml of ethanol, 1.51 ml of concentrated hydrochloric acid, and 1.51 g of ice. The mixture was allowed to stand for 12 h at 5°C, and the precipitate that formed was filtered off and recrystallized from aqueous ethanol. A white precipitate was obtained, mp 190°C, yield 47%, R_f 0.43. IR spectrum (Nujol), ν, cm^{-1}: 3250 (N–H), 1762 [C=O, $C_6H_5C(O)O$], 1680 [C=O, $NHC(O)C_6H_5$], 1620 sh (C=N), 1590, 1550, 1520, 1500 (C=C$_{arom}$). ^{1}H NMR specrum, δ, ppm: 7.03 s (1H, 4-CH), 7.2–8.0 m (12H, arom), 8.43 s (1H, 3-NH). Found, %: C 56.28; H 2.55; Cl 21.80. $C_{23}H_{14}Cl_3N_3O_3$. Calculated, %: C 56.73; H 2.87; Cl 21.89.

REFERENCES

1. Elguero, J., Marzin, C., Katritzky, A.R., and Linda, P., *The Tautomerism of Heterocycles,* New York: Academic, 1976.
2. Zolotov, Yu.A. and Kuz'min, N.M., *Ekstraktsiya metallov atsilpirazolonami* (Metal Extraction with Acylpyrazolones), Moscow: Nauka, 1977.
3. *The Theory of the Photographic Process,* James, T.H., Ed., New York: MacMillan, 1977, 4th ed.
4. Ono, S., Okazaki, K., Sakurai, M., and Inoue, Y., *J. Phys. Chem. A,* 1997, vol. 101, no. 20, p. 3769.
5. Katritzky, A.R. and Maine, F.W., *Tetrahedron,* 1964, vol. 20, p. 299.
6. Newman, G.A. and Pauwells, P.J.S., *Tetrahedron,* 1970, vol. 26, no. 13, p. 3429.
7. Maguestiau, A., Van Haverbeke, Y., and Jacguerye, R., *Bull. Soc. Chim. Belg.,* 1973, vol. 82, nos. 3–4, p. 233.
8. Okafor, E.C., *Spectrochim. Acta, Part A,* 1984, vol. 40, no. 5, p. 397.
9. Akama, Y., Shiro, M., Ueda, T., and Kajitani, M., *Acta Crystallogr., Sect. C,* 1995, no. 51, p. 1310.
10. Akama, Y. and Tong, A., *Microchem. J.,* 1996, vol. 53, no. 1, p. 34.
11. Ueda, T. and Akama, Y., *Chem. Phys. Lett.,* 1994, vol. 222, no. 4, p. 559.
12. Uzoukwu, B.A., *Spectrochim. Acta, Part A,* 1995, vol. 31, no. 6, p. 1081.

13. Uzoukwu, B.A., Al-Juaid, S.S., Hitchcock, P.B., and Smith, J.D., *Polyhedron,* 1993, vol. 12, p. 2719.
14. O'Connell, M.J., Ramsay, C.G., and Steel, P.J., *Aust. J. Chem.,* 1985, vol. 38, no. 3, p. 401.
15. Guard, J.A.M. and Steel, P.J., *Aust. J. Chem.,* 1994, vol. 47, no. 7, p. 1453.
16. *Cambridge Structural Database System,* Version 5.18, October 1999 Release.
17. Abdel-Hafez, Sh.H., Movchan, A.I., and Chmutova, G.A., *Chem. Comput. Simulation. Butlerov Commun.,* 2001, no. 4, OR4.
18 *Organikum,* Berlin: Wissenschaften, 1967, p. 396.
19. Levkoev, I.I., *Izbrannye trudy. Organicheskie veshchestva v fotograficheskikh protsessakh* (Selected Works. Organic Compounds in Photographic Processes), Moscow: Nauka, 1982.
20. Vilkov, L.V., Mastryukov, V.S., and Sadova, N.I., *Opredelenie geometricheskogo stroeniya svobodnykh molekul* (Determination of Geometric Structure of Free Molecules), Leningrad: Khimiya, 1978.
21. Naumov, V.A. and Kataeva, O.N., *Molekulyarnoe stroenie organicheskikh soedinenii kisloroda i sery v gazovoi faze* (Molecular Structure of Oxygen and Sulfur Organic Compounds in the Gas Phase), Moscow: Nauka, 1990.
22. Chmutova, G.A., Al'brekht, Kh., Aminova, R.M., and Leusheva, S.V., *Zh. Org. Khim.,* 1996, vol. 66, no. 8, p. 1346.
23. Altomare, A., Cascarano, G., Giacovazzo, C., and Viterbo, D., *Acta Crystallogr., Sect. A,* 1991, vol. 47, no. 4, p. 744.
24. Straver, L.H. and Schierbeek, A.J., *MolEN. Structure Determination System,* Program Description, Nonius B.V., 1994, vol. 1.
25. Spek, A.L., *Acta Crystallogr., Sect. A,* 1990, vol. 46, no. 1, p. 34.