

References

- BARANY, G. (1982). *Cryst. Struct. Commun.* **11**, 913–928.
 BARANY, G., SCHROLL, A. L., MOTT, A. W. & HALSRUD, D. A. (1983). *J. Org. Chem.* **48**, 4750–4761.
 BESTHORN, E. (1910). *Ber. Dtsch. Chem. Ges.* **43**, 1519–1526.

- Cambridge Structural Database (1983). May update. Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.
 FRENZ, B. A. (1978). In *Computing in Crystallography*, edited by H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Acta Cryst. (1984). **C40**, 2120–2122

2-Imino-*N*-phenyl-3-thiazolidinecarboxamide, C₁₀H₁₁N₃OS

BY C. R. RASMUSSEN, FRANK J. VILLANI JR AND ELIZABETH A. GRIFFIN

Department of Chemical Research, McNeil Pharmaceutical, Spring House, Pennsylvania 19477, USA

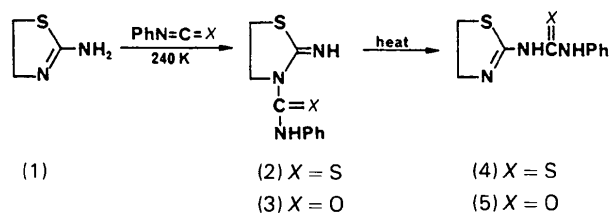
AND DAVID S. MORRISON AND R. A. OLOFSON

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

(Received 22 May 1984; accepted 29 August 1984)

Abstract. $M_r = 221.28$, orthorhombic, $P2_12_12_1$, $a = 7.550$ (2), $b = 12.684$ (3), $c = 22.095$ (3) Å, $V = 2116$ (1) Å³, $Z = 8$, $D_x = 1.389$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.79$ cm⁻¹, $F(000) = 928$, $T = 295$ K, $R = 0.072$ for 1625 observed reflections. The extremely labile kinetic adduct from reaction of 2-aminothiazoline with PhN=C=O has been identified thus also establishing several related structures. The geometry of the nearly flat molecule is determined by a hydrogen bond between the anilide NH and the imino nitrogen (imino NH not hydrogen-bonded to urea oxygen).

Introduction. Reaction of 2-amino-4,5-dihydrothiazole (1) with phenyl isothiocyanate was first reported (Fromm & Kapeller-Adler, 1928) to give a low-melting adduct (2) which rearranged on melting (or more easily in solution) to an isomer (4). Later workers failed to find the low-melting adduct and assigned structure (2) to the high-melting isomer (m.p. 421 K) based on an 'unequivocal synthesis' (Klayman, Maul & Milne, 1967). In a subsequent retraction, the m.p. 421 K isomer was reassigned structure (4) (Klayman, Maul & Milne, 1968). A similar product (depicted as 5) was obtained (no 3 found) in the analogous treatment of (1) with phenyl isocyanate (Klayman, Maul & Milne, 1968). As part of a major investigation of the pharmaceutical utility of 2-pyrrolidinyldene ureas (Rasmussen, Gardocki, Plampin, Twardzik, Reynolds, Molinari, Schwartz, Bennetts, Price & Marakowski, 1978) and aryl urea derivatives of creatinine, the reactions of (1) with both PhN=C=S and PhN=C=O have been repeated and compounds identified as (2)–(5) isolated. All four structure proofs rest in part on the single-crystal X-ray structure analysis of the very unstable (3) presented here.



Experimental. Irregularly shaped crystal (0.25 × 0.2 × 0.3 mm) cleaved from larger crystal grown from ether–hexane at 195 K (Rasmussen, Villani, Mutter & Griffin, 1984); unit-cell parameters from 25 reflections in θ range 1.6–30°; Enraf–Nonius CAD-4 diffractometer (graphite monochromator); systematic absences $h00$ h odd, $0k0$ k odd, $00l$ l odd; data corrected for Lorentz and polarization factors but not for absorption; max. $2\theta = 60^\circ$, h, k, l max. 10, 17, 31; variable scan rate; three standard reflections every 1 h (anisotropic decay correction: 0.974–1.060, av. correction = 1.019); 3706 reflections measured, 2733 unique, 1108 unobserved [$I < 1.75\sigma(I)$]; structure by direct methods using *MULTAN78* (Main, Hull, Lesinger, Germain, Declercq & Woolfson, 1978) with all non-H atoms refined anisotropically on F ; H(N1) and H(N3) found by difference Fourier maps and their positions refined; remaining H atoms placed in calculated positions ($B_{\text{iso}} = 5.0$ Å²); 283 parameters refined; $R = 0.072$, $wR = 0.068$, $S = 1.33$; Corfield, Doedens & Ibers (1967) weighting scheme with $p = 0.07$ and $w = F^2/\sigma^2(F^2)$; max. $\Delta/\sigma = 0.02$; max. height in final difference Fourier map = 0.212 e Å⁻³; f, f' from Cromer & Waber (1974); programs: *MULTAN78*, *SDP Plus* version 1.0 (Enraf–Nonius, 1979), *ORTEPII* (Johnson, 1976).

Table 1. Atomic coordinates and B_{eq} values (\AA^2)

Molecule	$B_{eq} = \frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33}]$			B_{eq}
	x	y	z	
Molecule A				
S(1)	1.1044 (2)	0.5140 (1)	0.6472 (1)	4.9
O(1)	0.8042 (6)	0.7508 (3)	0.7844 (2)	4.8
N(1)	1.0366 (8)	0.4569 (4)	0.7631 (2)	4.9
N(2)	0.9458 (6)	0.6230 (3)	0.7308 (2)	3.4
N(3)	0.8686 (7)	0.5951 (4)	0.8313 (2)	4.1
C(1)	1.0249 (8)	0.5248 (4)	0.7224 (2)	3.5
C(2)	0.9449 (10)	0.6913 (5)	0.6781 (3)	3.9
C(3)	1.0024 (14)	0.6359 (6)	0.6259 (3)	7.7
C(4)	0.8671 (7)	0.6630 (4)	0.7835 (2)	3.2
C(5)	0.7829 (8)	0.6100 (5)	0.8874 (2)	3.8
C(6)	0.7224 (12)	0.7058 (5)	0.9088 (3)	6.0
C(7)	0.6423 (12)	0.7096 (6)	0.9647 (3)	6.2
C(8)	0.6194 (11)	0.6232 (6)	0.9996 (3)	6.6
C(9)	0.6801 (11)	0.5277 (6)	0.9784 (3)	6.3
C(10)	0.7612 (10)	0.5205 (5)	0.9226 (3)	5.1
Molecule B				
S(1')	0.6155 (3)	0.4224 (1)	0.6379 (1)	5.4
O(1')	0.5469 (7)	0.2240 (3)	0.8226 (2)	5.4
N(1')	0.4926 (9)	0.5162 (4)	0.7402 (2)	4.9
N(2')	0.5855 (7)	0.3398 (3)	0.7451 (2)	3.8
N(3')	0.4442 (8)	0.3920 (4)	0.8338 (2)	4.7
C(1')	0.5557 (8)	0.4352 (5)	0.7145 (3)	4.2
C(2')	0.6448 (9)	0.2532 (5)	0.7070 (3)	4.5
C(3')	0.7305 (10)	0.2993 (5)	0.6510 (3)	6.1
C(4')	0.5252 (9)	0.3144 (5)	0.8030 (3)	4.4
C(5')	0.3610 (9)	0.3898 (5)	0.8902 (3)	4.3
C(6')	0.3610 (10)	0.3027 (5)	0.9280 (3)	5.1
C(7')	0.2723 (12)	0.3076 (6)	0.9833 (3)	6.6
C(8')	0.1892 (11)	0.3972 (7)	1.0011 (3)	7.0
C(9')	0.1889 (11)	0.4854 (6)	0.9637 (3)	6.7
C(10')	0.2733 (11)	0.4804 (5)	0.9092 (3)	5.7

Discussion. Atomic positional parameters are listed in Table 1.* Significant bond distances and angles are in Fig. 1 with the crystallographic numbering system and a stereoview of adjacent molecules is shown in Fig. 2. Both unique molecules (*A* and *B*) are nearly planar; the dihedral angle between plane *P1* [C(5)–C(10)] and plane *P2* [N(1), C(1), N(2), C(4), O(1), N(3)] is 14.6° in *A* and 5.7° in *B*. While S(1) is in plane *P2A* (deviation 0.007 Å), S(1') is 0.31 Å from plane *P2B*. Surprisingly, the molecule chooses a conformation (*3a*) in which the anilide NH is hydrogen-bonded to the imino nitrogen. The expected geometry in which the imino NH is hydrogen-bonded to the more basic urea oxygen (*3b*) is not found (note: in both *3a* and *3b*, the phenyl moiety is in the normal position *vs* H in the secondary amide). We ascribe the preference for (*3a*) over (*3b*) to a greater destabilizing dipole repulsion between C=N and C=O in (*3b*). In the packing of *A* and *B*, an attraction between antiparallel C=O dipoles is evident; also the phenyl and thiazolidine rings in *A* and *B* are nearly parallel: $P1A \wedge P1B = 9.6^\circ$, $P2A \wedge P2B = 6.7^\circ$ (for a similar effect see Wooden, Hoskin & Olofson, 1981).

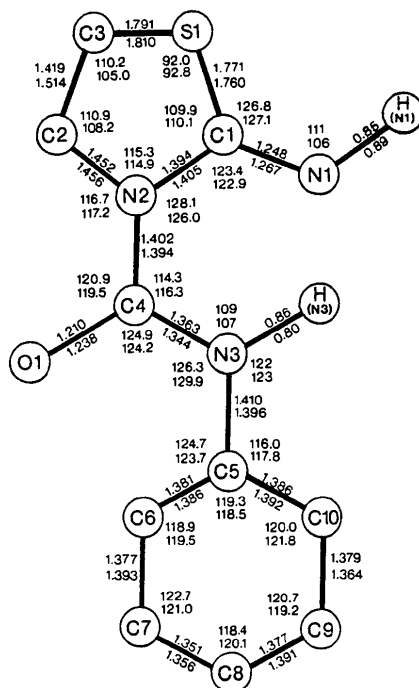
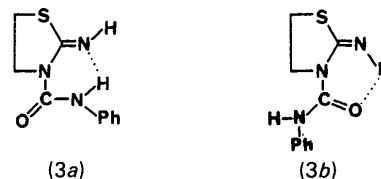


Fig. 1. Crystallographic numbering system with bond distances (Å) and angles ($^\circ$) for non-H atoms (e.s.d. ranges are 0.006–0.011 Å and 0.3–0.7 $^\circ$). The upper value refers to molecule *A*.

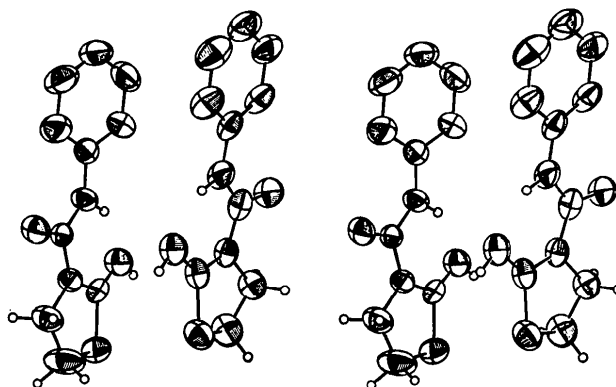


Fig. 2. Stereoscopic view of adjacent molecules (*B* on left). Thermal ellipsoids for non-H atoms represent 50% probability (phenyl H atoms omitted for clarity); C(6) is closest to O(1).

* Lists of complete bond distances and angles, hydrogen positional parameters, least-squares planes, anisotropic thermal parameters, structure factors and a unit-cell stereoview have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39700 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

We thank Drs R. R. Whittle and G. P. Wooden for useful discussions.

References

- CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press.
- Enraf-Nonius (1979). *Structure Determination Package*. Enraf-Nonius, Delft.
- FROMM, E. & KAPPELLER-ADLER, R. (1928). *Justus Liebig's Ann. Chem.* **467**, 240–274.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KLAYMAN, D. L., MAUL, J. J. & MILNE, G. W. (1967). *Tetrahedron Lett.* pp. 281–284.
- KLAYMAN, D. L., MAUL, J. J. & MILNE, G. W. (1968). *J. Heterocycl. Chem.* **5**, 517–522.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- RASMUSSEN, C. R., GARDOCKI, J. F., PLAMPIN, J. N., TWARDZIK, B. L., REYNOLDS, B. E., MOLINARI, A. J., SCHWARTZ, N., BENNETTS, W. W., PRICE, B. E. & MARAKOWSKI, J. (1978). *J. Med. Chem.* **21**, 1044–1054.
- RASMUSSEN, C. R., VILLANI, F. J. JR, MUTTER, M. S. & GRIFFIN, E. A. (1984). In the press.
- WOODEN, G. P., HOSKIN, D. H. & OLOFSON, R. A. (1981). *Acta Cryst.* **B37**, 722–724.

Acta Cryst. (1984). **C40**, 2122–2124

A Polarized Twisted Ethylene: (1,3-Dimethyl-2-imidazolidinylidene)phenylacetonitrile, C₁₃H₁₅N₃

BY NIRUPA SEN (NÉE KAMATH) AND K. VENKATESAN

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

AND K. R. ACHARYA AND T. N. GURU ROW

National Chemical Laboratory, Poona 411 007, India

(Received 4 June 1984; accepted 3 September 1984)

Abstract. $M_r = 213.13$, orthorhombic, $P2_12_12_1$, $a = 9.858$ (2), $b = 10.951$ (2), $c = 10.984$ (2) Å, $V = 1185.8$ Å³, $Z = 4$, $D_m = 1.191$ (2) (by flotation method in KI solution), $D_x = 1.194$ (2) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.41$ cm⁻¹, $F(000) = 456$, $T = 293$ K. Final $R = 0.041$ for 875 significant reflections. The C=C bond length is 1.382 (4) Å, significantly longer than that in ethylene, 1.336 (2) Å. The molecule is twisted about the C=C bond by 23.1 (4)° and the phenyl group is rotated out of the plane of this bond by 39.4 (4)°. Molecular packing is determined by van der Waals forces.

Introduction. Polarized twisted ethylenes having donors such as the 1,3-dimethyl-2-imidazolidinylidene ring and phenyl and cyano groups as acceptors have been investigated by X-ray crystallography (Adhikesavalu, Kamath & Venkatesan, 1983; Abrahamsson, Rehnberg, Liljefors & Sandström, 1974; Sen & Venkatesan, 1984).

We have now investigated the molecular structure of (1,3-dimethyl-2-imidazolidinylidene)phenylacetonitrile with a strong donor and weak acceptor combination.

Experimental. Single crystals of title compound obtained from toluene by slow evaporation, approximate dimensions 0.2 × 0.4 × 0.6 mm. Preliminary Weissenberg photographs indicated that the crystals are orthorhombic. Lattice parameters refined using a least-squares fit to the settings for 25 accurately centered reflections. Nonius CAD-4-11M diffractometer, monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, $\theta \leq 24^\circ$. During data collection three standard reflections (400, 004, 123) showed only statistical variation within $\pm 2\%$. 1141 reflections collected, hkl range: h 0 to 11, k 0 to 12, l 0 to 12, 875 significant, $|F_o| \geq 3\sigma(|F_o|)$. Data not corrected for absorption. Structure solved by direct methods (*MULTAN80*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement (*SHELX76*; Sheldrick, 1976) of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged to $R = 0.041$, $R_w = 0.037$, $S = 1.97$; $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1.2213 / [\sigma^2(F) + 0.00002|F_o|]$. Δ/σ for non-H atoms ~ 0.001 . Final difference map featureless. Atomic scattering