tation were performed using *TEXSAN* (Molecular Structure Corporation, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with stereo molecular and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71667 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1057]

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Intermolecular Hydrogen-Bonded Structure of Bis(4-methoxyphenylmethine)carbonohydrazide

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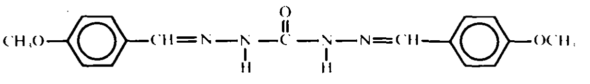
Abstract

The first reported X-ray crystal structure of a carbazone is described. [For a discussion of CAS/IUPAC nomenclature of carbazones see Grasselli & Weast (1989). In *Handbook of Data on Organic Compounds*, 2nd edition, Vol. I, Introduction, §§190, 252. Florida: CRC Press.] Crystalline 1,5-bis(4-methoxyphenylmethine)carbonohydrazide, (I), $C_{17}H_{18}N_4O_3$, exists as a non-centrosymmetric infinite hydrogen-bonded chain in which both amidic H atoms of one molecule are tightly hydrogen bonded to the carbonyl O atom of another molecule, forming intermolecular six-membered ring linkages. The intermolecular hydrogen-bond distances for N—H···O are 1.91 Å for H···O and 2.759 (5) Å for N···O, and the N—H···O angles are 148.0°.

Comment

IR spectra of a series of semicarbazones in the solid state were found to exhibit unexpectedly high carbonyl frequencies (Kolb, Stupar, Janota & Duax, 1989; Kolb, Janota, Dantzman, Kozenski, Strommen, Snyder & Tipsword, 1992). Through a combination of Raman spectroscopic and X-ray crystallographic studies these unpredicted frequency shifts were attributed to vibrational coupling of the C=O bands in the solid-state hydrogen-bonded network (Kolb, Janota, Dantzman, Kozenski, Strommen, Snyder & Tipsword, 1992; Kolb, Dantzman, Kozenski & Strommen, 1993). The Raman and IR carbonyl frequencies of a series of related carbazones in the solid state were then examined in an attempt to deduce their structure (Kolb, Janota, Dantzman, Kozenski & Strommen, 1992). To investigate more specifically the role played by hydrogen bonding and to correlate the carbonyl frequencies with patterns of hydrogen bonding, we undertook X-ray studies of the crystal structures of these carbazones (Kolb, Meyers & Robinson, 1993). Although the crystal structure of carbazide itself, $NH_2NHC(O)NHNH_2$, has been studied by X-ray diffraction (Domiano, Pellinghelli & Tiripicchio, 1972) and more recently by neutron diffraction (Jeffrey, Ruble, Nanni, Turano & Yates, 1985), no X-ray structure of a carbazone has been reported previously. We describe here the intermolecular hydrogen-bonded crystal structure of bis(4-methoxyphenylmethine)carbonohydrazide (I).



(I)

A solution of 762 mg (5.6 mmol) of *p*-methoxybenzaldehyde and 250 mg (2.8 mmol) of carbazide in 20 ml of ethanol was refluxed overnight. The cooled solution yielded a mass of colorless crystals of (I) which were collected by filtration and recrystallized from ethanol to a constant melting point, 479-482 K. The well defined pattern of intermolecular hydrogen bonding in the crystal structure of (I) is shown in Fig. 1 and the spatial orientation of the hydrogen-bonded molecules is illustrated in Fig. 2.

Several important structural features are exhibited. (1) The individual molecules have an essentially planar and symmetrical conformation in which the amidic N atoms are trigonal and the amidic H atoms are *anti* to the carbonyl O atom. (2) Both amidic H atoms of one molecule are identically hydrogen bonded to the carbonyl O atom of another molecule (*e.g.* N2—H6 and N2^{ii}—H6^{ii} to O1^{i}=C8^{i}), forming a six-membered ring as the intermolecular linkage. This type of amidic hydrogen-bonding pattern is also found in the crystal structure of urea (Vaughan & Donohue, 1952) and that of the complex of urea with barbital (Gartland & Craven, 1974; Hsu & Craven, 1974). (3) All the molecules are interconnected through these hydrogen-bonded linkages in a non-centrosymmetric infinite chain; no other atoms are involved in hydrogen bonding. (4) The intermolecular hydrogen-bond distances of N—H···O are 1.91 Å for H···O and 2.759 (5) Å for N···O and the angles are 148.0°. (5) The linked molecules form a three-dimensional 'X' pattern (Fig. 2) which indicates that a significant part of the hydrogen bonding involves the π-orbital electrons of the O=C bonds.

Crystal structure determinations of related carbazones are now underway. The relationship between their hydrogen-bonding patterns and the carbonyl frequencies in their Raman and IR spectra will be described elsewhere.

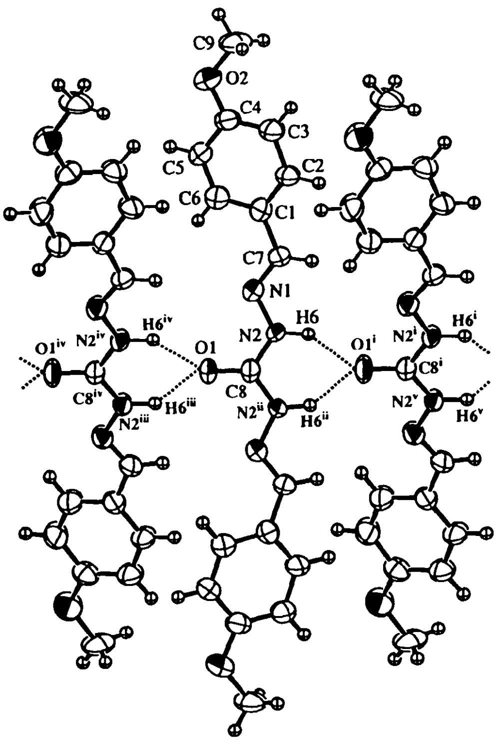


Fig. 1. Molecular configuration, hydrogen bonding and atomic numbering scheme with thermal ellipsoids at the 50% probability level. H atoms are shown as unlabeled isotropic spheres of arbitrary radii. Superscripts (i), (ii), (iii), (iv) and (v) refer to atom designator codes 65502, 65507, 55508, 65407 and 55408, respectively (Johnson, 1965). The top half of each molecule is related to the bottom half by a twofold axis of symmetry which passes through the O1 and C8 atoms. The molecule on the left is related to the molecule on the right by a unit translation along the *c* axis.

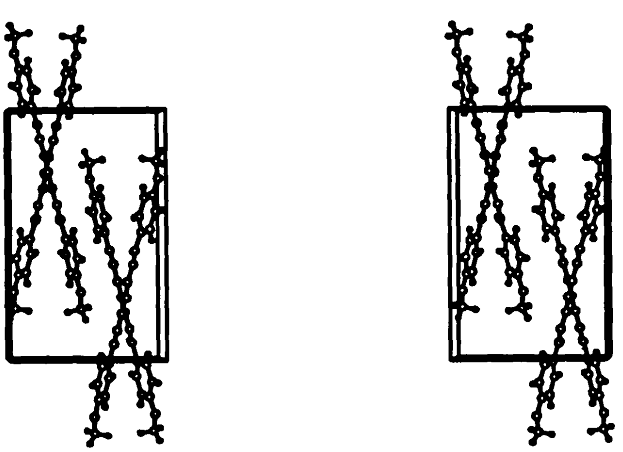


Fig. 2. Stereoscopic illustration of the molecular packing. The origin is at the lower-left-back corner, *a* is horizontal, *b* is vertical and *c* is out of the plane of the paper. The infinite hydrogen-bonded chains propagate in the direction of the *c* axis.

Experimental

Crystal data

$C_{17}H_{18}N_4O_3$
M_r = 326.35
Orthorhombic
Pccn
a = 10.689 (1) Å
b = 17.448 (3) Å
c = 8.976 (1) Å
V = 1674.2 (4) Å^3
Z = 4
D_x = 1.295 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 23 reflections
θ = 3.2-10.1°
μ = 0.085 mm^{-1}
T = 296 K
Prism
0.38 × 0.24 × 0.11 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
1736 measured reflections
1736 independent reflections
608 observed reflections [$I > 3.0\sigma(I)$]

θ_{max} = 25°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 100 reflections
intensity variation: 0.6%

Refinement

Refinement on F
R = 0.045
wR = 0.057
S = 1.80
608 reflections
111 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.0007
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 0.16 (2) × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
O1	3/4	1/4	0.2876 (5)	0.059 (2)
O2	0.5405 (4)	0.7260 (2)	0.2704 (4)	0.072 (1)
N1	0.6973 (4)	0.3813 (2)	0.1372 (4)	0.047 (1)
N2	0.7294 (4)	0.3135 (2)	0.0680 (3)	0.049 (1)
C1	0.6413 (4)	0.5134 (3)	0.1071 (5)	0.047 (2)
C2	0.6480 (5)	0.5757 (3)	0.0160 (5)	0.053 (2)
C3	0.6151 (4)	0.6499 (3)	0.0651 (6)	0.053 (2)
C4	0.5732 (5)	0.6585 (3)	0.2093 (6)	0.051 (2)
C5	0.5596 (6)	0.5935 (3)	0.3007 (6)	0.064 (2)
C6	0.5942 (5)	0.5237 (3)	0.2496 (6)	0.059 (2)
C7	0.6789 (5)	0.4379 (2)	0.0499 (6)	0.047 (2)
C8	3/4	1/4	0.1516 (7)	0.045 (2)
C9	0.5463 (6)	0.7936 (3)	0.1773 (6)	0.071 (2)
H6	0.7370	0.3114	−0.0374	0.059

Table 2. *Selected geometric parameters* (Å, °)

O1—C8	1.222 (6)	C1—C7	1.471 (6)
O2—C4	1.346 (5)	C2—C3	1.412 (6)
O2—C9	1.446 (5)	C3—C4	1.377 (6)
N1—N2	1.379 (4)	C4—C5	1.408 (7)
N1—C7	1.276 (5)	C5—C6	1.352 (6)
N2—C8	1.357 (4)	N2—H6	0.95
C1—C2	1.362 (6)	H6—O1$^{\rm i}$	1.91
C1—C6	1.387 (7)	N2—O1$^{\rm i}$	2.759 (5)
C4—O2—C9	117.9 (4)	O2—C4—C5	116.2 (5)
N2—N1—C7	115.1 (4)	C3—C4—C5	119.6 (5)
N1—N2—C8	119.5 (3)	C4—C5—C6	119.9 (5)
C2—C1—C6	118.0 (5)	C1—C6—C5	122.0 (5)
C2—C1—C7	119.4 (4)	N1—C7—C1	121.4 (4)
C6—C1—C7	122.6 (4)	O1—C8—N2	123.6 (3)
C1—C2—C3	122.1 (5)	N2—C8—N2$^{\rm ii}$	112.9 (5)
C2—C3—C4	118.3 (5)	N2—H6—O1$^{\rm i}$	148.0
O2—C4—C3	124.3 (5)		

Symmetry codes: (i) $\frac{3}{2} - x, y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, \frac{1}{2} - y, z$.

The scan rate was 4° min^{-1} (in ω). Weak reflections [$I < 10\sigma(I)$] were rescanned (maximum of three rescans) and the counts accumulated to improve accuracy. H atoms were placed at assumed positions (C,N—H = 0.95 Å, $U = 1.2 \times U_{\rm eq}$ of the associated atom) and fixed. Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN*, *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71656 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1083]

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(2*E*,4*E*,6*E*)-7-(6-Méthyl-2*H*-1-benzopyran-3-yl)hepta-2,4,6-triénoate d'Ethyle

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Abstract

The effects of retinoids on cell differentiation and proliferation, as well as on the inflammatory process, have been well documented, but so far their clinical use has been affected by teratogenicity and hypervitaminosis A [Loeliger, Bollag & Maier (1980). *Eur. J. Med.* **15**, 9-15]. The need for safer drugs

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