

one face likewise has four intra-annular H atoms; the shortest non-bonded H...H distances (Table 2) are comparable to those observed in cyclododecane and in azacyclododecane hydrochloride (Dunitz & Weber, 1964). The other face, however, has two opposing nitrogen lone pairs. The facts that the N(1)...N(9) transannular distance is shorter than the C(17)...C(18) distance and C(4)...C(12) is shorter than C(3)...C(11) are direct reflections of the smaller van der Waals radius of nitrogen relative to that of methylene (Riddell, 1980b) (Table 2; see also the related H...H transannular distances). The decreased strain may also be part of the reason for the relatively normal C—C—N and C—N—C bond angles at the corners of the [3333] conformation. Corner bond angles in cyclododecane (Dunitz & Shearer, 1960) are considerably expanded compared to those observed in this work.

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Structure of 1-(4-Chlorobenzylidene)-5,5-dimethyl-3-pyrazolidone Betaine, C₁₂H₁₃ClN₂O*

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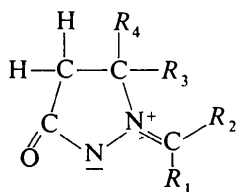
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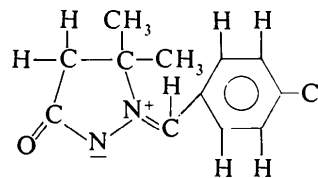
(Received 1 February 1982; accepted 1 October 1982)

Abstract. $M_r = 236.7$, monoclinic, $P2_1/n$, $a = 9.079$ (4), $b = 18.576$ (10), $c = 7.205$ (5) Å, $\beta = 94.26$ (2)°, $Z = 4$, $V = 1211.8$ (8) Å³, $D_x = 1.297$ (1) Mg m⁻³, $F(000) = 496$, $\mu(\text{Mo } K\alpha) = 0.302$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $T = 296$ K. Final $R = 0.059$ for 2116 independent reflections excluding those with $|F_o| < 4\sigma(F_o)$. The azomethine imine unit of the molecule has a geometry in approximate agreement with a polymethine-like electronic structure. The whole molecule is approximately planar. Conjugation of the azomethine imine unit with the phenyl unit is indicated. There are some indications of intermolecular C—H...O hydrogen bridges.

Introduction. The compound (C₁₂H₁₃ClN₂O), abbreviated as CDPB, belongs to the class of azomethines of general formula (1) and is formally an azomethine-3 dipole (Huisgen, 1963) with the complete formula (2). The structures of the related 1-(4-nitrobenzylidene)-3-pyrazolidone betaine, NPB (Kulpe, Seidel, Geissler &



(1)



(2)

* Structures of Azomethine Imines of the 3-Pyrazolidone Type. II. Part I: Kulpe, Seidel, Geissler & Tomaschewski (1981).

Tomaschewski, 1981), 1-(4-methoxybenzylidene)-3-pyrazolidone betaine, MPB (Kulpe, Seidel & Geissler, 1982a) and 1-(9-anthrylmethylene)-3-pyrazolidone betaine, AMPB (Kulpe, Seidel & Geissler, 1982b) have been reported.

The object of the investigation is to find relations between the molecular geometry, the conformation and intermolecular packing, on the one hand, and photochromic and biochemical behaviour on the other. IR spectroscopic (Dorn & Otto, 1968; Siegmund, Schleinitz, Menz & Geissler, 1981) and UV/visible spectroscopic results (Tomaschewski, Geissler & Schauer, 1980) have been reported. In (1) and (2) we use canonical structures with some degree of consistency with the X-ray data.

Experimental. Preparation as reported (Geissler, Angermueller, Behning, Fuernissen, Fust, Hippins, Mueller, Schauer, Slezak & Tomaschewski, 1981), yellow prisms, $1.0 \times 0.3 \times 0.5$ mm, by cooling hot benzene solution, sensitive to mechanical stress, Hilger & Watts diffractometer, graphite-monochromatized Mo $K\alpha$, lattice parameters from diffractometer settings, 2776 unique reflections (hkl and $\bar{h}\bar{k}\bar{l}$), $2\theta < 55^\circ$, 2116 with $|F_o| \geq 4\sigma(|F_o|)$, e.s.d.'s from counter statistics, ω - 2θ step scan, 50 steps of $1s$, $\Delta\omega = 0.02^\circ$, systematic extinctions $h0l$ for $h+l$ odd and $0k0$ for k odd, L_p

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and some of the intramolecular bond lengths and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38159 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional coordinates ($\times 10^4$) and equivalent isotropic ($\text{\AA}^2 \times 10^3$) thermal parameters with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3 \sin^2 \beta} (U_{11} + U_{22} \sin^2 \beta + U_{33} + 2U_{13} \cos \beta) \text{ (Hamilton, 1959).}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cl(1)	492 (1)	4463 (1)	2915 (2)	103 (1)
O(1)	6612 (3)	6889 (1)	-3672 (3)	90 (1)
N(1)	6355 (2)	6613 (1)	0899 (3)	53 (1)
N(2)	5859 (2)	6507 (1)	-0903 (3)	58 (1)
C(1)	6791 (3)	6867 (2)	-1972 (4)	64 (1)
C(2)	7999 (3)	7244 (2)	-0840 (4)	78 (1)
C(3)	7707 (3)	7104 (2)	1176 (4)	59 (1)
C(4)	5721 (3)	6350 (2)	2302 (4)	58 (1)
C(5)	4444 (3)	5891 (2)	2321 (4)	57 (1)
C(6)	3619 (3)	5628 (2)	0758 (4)	71 (2)
C(7)	2416 (4)	5191 (2)	0976 (5)	80 (2)
C(8)	2009 (3)	5022 (1)	2689 (5)	73 (2)
C(9)	2790 (3)	5271 (2)	4277 (5)	76 (2)
C(10)	3998 (3)	5708 (2)	4056 (4)	67 (2)
C(11)	7279 (4)	7779 (2)	2177 (4)	78 (2)
C(12)	8930 (4)	6699 (2)	2256 (5)	84 (2)

Table 2. Intramolecular bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Cl(1)-C(8)	1.742 (3)	C(3)-C(11)	1.511 (4)
O(1)-C(1)	1.224 (3)	C(3)-C(12)	1.508 (5)
N(1)-N(2)	1.357 (3)	C(4)-C(5)	1.440 (4)
N(1)-C(3)	1.531 (3)	C(5)-C(6)	1.393 (4)
N(1)-C(4)	1.296 (3)	C(6)-C(7)	1.381 (5)
N(2)-C(1)	1.362 (3)	C(7)-C(8)	1.351 (4)
C(1)-C(2)	1.491 (4)	C(8)-C(9)	1.380 (5)
C(2)-C(3)	1.518 (4)	C(9)-C(10)	1.383 (4)
		C(5)-C(10)	1.391 (4)
N(2)-N(1)-C(3)	114.7 (2)	C(11)-C(3)-C(12)	111.9 (3)
N(2)-N(1)-C(4)	123.8 (2)	N(1)-C(4)-C(5)	129.4 (2)
C(3)-N(1)-C(4)	121.4 (2)	C(4)-C(5)-C(6)	125.7 (2)
N(1)-N(2)-C(1)	107.1 (2)	C(4)-C(5)-C(10)	116.2 (2)
N(2)-C(1)-O(1)	122.7 (2)	C(6)-C(5)-C(10)	118.1 (2)
N(2)-C(1)-C(2)	112.6 (2)	C(5)-C(6)-C(7)	119.7 (3)
O(1)-C(1)-C(2)	124.7 (3)	C(6)-C(7)-C(8)	120.9 (3)
C(1)-C(2)-C(3)	105.6 (2)	Cl(1)-C(8)-C(7)	119.7 (2)
N(1)-C(3)-C(2)	99.9 (2)	Cl(1)-C(8)-C(9)	118.9 (3)
N(1)-C(3)-C(11)	108.9 (2)	C(7)-C(8)-C(9)	121.4 (3)
N(1)-C(3)-C(12)	108.8 (2)	C(8)-C(9)-C(10)	117.9 (3)
C(2)-C(3)-C(11)	112.6 (2)	C(5)-C(10)-C(9)	122.0 (3)
C(2)-C(3)-C(12)	113.6 (3)		

correction, absorption ignored, no significant variation in standard reflections, direct methods, *SHELX* (Sheldrick, 1976), full-matrix least-squares of positional and anisotropic thermal parameters minimizing $\sum w(\Delta|F|)^2$, H (from difference ρ) isotropic, final $R = 0.059$,* unit weights, scattering factors from *International Tables for X-ray Crystallography* (1974), BESM computer. Positional parameters are in Table 1, bond lengths and angles in Table 2.

Discussion. In all essential details, the molecular geometry of CDPB (Fig. 1) is very similar to those of NPB and MPB. Hence the electronic structures of the three compounds are very similar. The important bond length $C(4)-C(5) = 1.440$ (4) \AA [in NPB 1.448 (3) \AA , in MPB 1.440 (3) \AA] is slightly shorter than the standard single-bond length $C(sp^2)-C(sp^2) = 1.47$ \AA indicating conjugation of the azomethine imine unit to the phenyl unit. The assumption of a change of hybridization of the methylene carbon atom C(4) has been suggested in the course of the photoreaction (Tomaschewski, Geissler & Schauer, 1980).

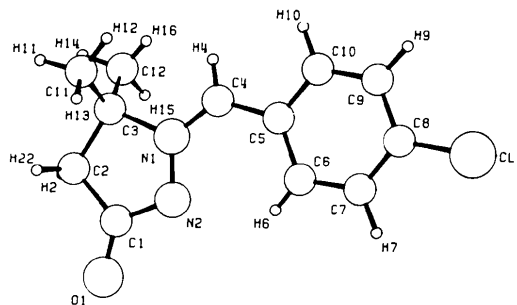
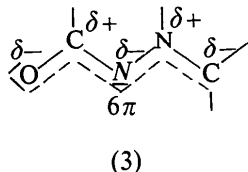


Fig. 1. Numbering scheme of the atoms in the molecule.

The proposed polymethine concept (Dähne & Kulpe, 1977) seems to be useful for understanding the geometry and the electronic structure of the compound. The azomethine imine unit can be described in terms of (3).



The main feature of this proposal is: along the chain of five atoms O, C, N, N, C about six π electrons are delocalized and the atoms of the polymethinic chain, in particular the three inner atoms, have partial alternating π charges with signs as in (3). Thus the whole molecule may be considered to consist of an azomethine imine unit with polymethinic character and a phenyl unit with aromatic character, linked together by the bond C(4)–C(5). This holds for CDPB as well as for NPB. Because of the short bond length N(1)–C(4) = 1.296 (3) Å [NPB 1.303 (3) Å, MPB 1.289 (3) Å] a positive charge at the N(1) atom has to be assumed. The mean value of bond lengths found for the carbonyl group in the structures NPB, CDPB, MPB and AMPB (Kulpe, Seidel, Geissler & Tomaschewski, 1981; Kulpe, Seidel & Geissler, 1982*a,b*) is 1.233 (10) Å. There seem to be some specific properties associated with this *polymethinic carbonyl group* (Kulpe, 1980, 1981).

The maximum deviation from the mean plane through the atoms C(5), C(6), C(7), C(8), C(9), C(10) of the phenyl ring is 0.006 (3) Å. The mean plane through the atoms N(1), N(2), C(1), C(2), C(3) of the five-membered ring shows approximate planarity of this ring, maximum deviation from the plane is 0.018 (8) Å. The dihedral angle between the two planes is 1.6 (4)°, showing the possibility of conjugation too. In NPB an angle of 19.5 (4)° (in MPB exactly 0°) is observed. Thus the whole molecule is approximately planar. A closer examination of the five-membered ring reveals a slight envelope conformation, Fig. 2.

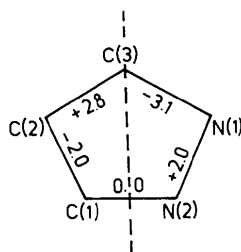


Fig. 2. Envelope conformation of the five-membered ring with torsion angles (°); e.s.d.'s are 0.4°.

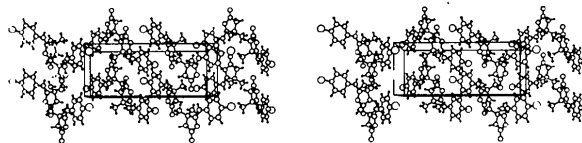
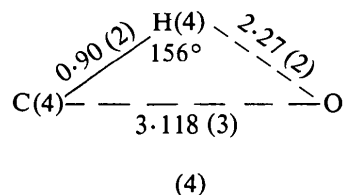


Fig. 3. Stereoscopic view, down the *a* axis, of the packing of the molecules.

Fig. 3 shows a stereoscopic view of the molecular packing. Intermolecular short C–H...O contacts (possible hydrogen bridges) link rows of molecules along the *c* axis. The geometry is illustrated in (4). The existence of such short contacts indicates a significant electronegativity of the C(4) atom (Kulpe & Seidel, 1982). The geometry of the chlorobenzyl substituent is similar to that of chlorobenzene (André, Fourme & Renaud, 1971).



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