

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 JARCHOW, O. H. (1969). *Acta Cryst.* B25, 267–275.  
 LONG, R. E. (1965). *A Program for Phase Determination by Reiterative Application of Sayre's Equation*. Ph. D. Thesis, UCLA.

MASON, R. (1961). *Acta Cryst.* 14, 720–724.  
 PAULUS, H. (1966). Ph. D. Dissertation, Technische Hochschule, Darmstadt.  
 SERES, J. (1970). *Investigations in the Field of Substituted Succinimides*. Dr Techn. Thesis, Technical Univ., Budapest.  
*X-RAY-63 Program System for X-ray Crystallography* (1964). Department of Chemistry, Univ. of Washington, Seattle and Univ. of Maryland, College Park.

*Acta Cryst.* (1973). B29, 1190

## The Crystal and Molecular Structure of 2-Phenyl-4-(4-bromophenyl)-5,6-dimethyl-5,6-dihydro-4*H*-1,3-oxazine, C<sub>18</sub>H<sub>18</sub>NOBr

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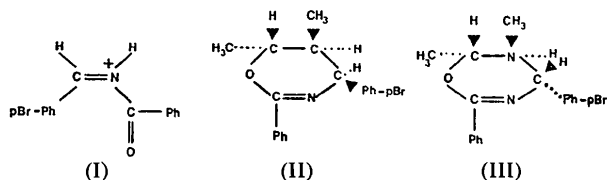
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C<sub>18</sub>H<sub>18</sub>NOBr is monoclinic, space group  $P2_1/c$ , with  $a=11.985$  (6),  $b=18.576$  (11),  $c=7.260$  (6) Å,  $\beta=94.6$  (1)° and  $Z=4$ . The three-dimensional intensity data were collected on a single-crystal automated diffractometer (1651 observed structure factors). The structure was solved by Patterson and Fourier syntheses and refined by the least-squares method. The final  $R$  value, with isotropic hydrogen atoms, is 0.062. The heterocyclic ring is in a *trans-syn* configuration, with the two methyl groups *equatorial* and *trans*, while the bromophenyl substituent is *axial* and *syn* with respect to the adjacent methyl group. A survey of the bond lengths suggests a weak delocalization of the C(4)–N double bond to the other bonds to which C(4) contributes. The conformation of the oxazine ring is the 'half-boat' type, with five atoms nearly planar and one, C(2), out of plane. Molecules are packed with van der Waals contacts.

### Introduction

In the reaction between benzonitrile and *p*-bromobenzaldehyde in acetic acid solution, catalyzed by H<sub>2</sub>SO<sub>4</sub> (Schmidt, 1970; Giordano, Ribaldone & Borsotti, 1971) the formation of an amidomethyl ion (I) can be hypothesized. Its reaction with *trans*-butene gives two oxazine diastereomers (II) and (III), by means of a stereospecific 1,4-cycloaddition on the olefin.



The two products are in the ratio 4:1 and can be identified as *trans-syn* and *trans-anti* configurations.\*

An X-ray structural determination of the oxazine obtained should give confirmation of n.m.r. configurational and conformational studies of these compounds (Giordano & Abis, 1973) and of corresponding thia-

zines (Abis & Giordano, 1973), and seemed useful in a class of heterocyclic compounds where no crystallographic literature was found.

### Experimental

Colourless prismatic crystals were provided by Dr C. Giordano of the Organic Chemistry Research Centre, Montecatini Edison Co., Novara. For crystallographic measurements, a crystal was cut of dimensions approximately 0.15 × 0.3 × 0.4 mm. The unit-cell dimensions were determined from rotation and Weissenberg photographs and refined by a least-squares analysis of 12 reflexions on a four circle automated Picker diffractometer, using Mo  $K\alpha$  radiation ( $\lambda=0.71609$  Å). Weissenberg photographs showed the space group extinctions  $k=2n+1$  for  $0k0$  and  $l=2n+1$  for  $h0l$ ; the space group was therefore  $P2_1/c$ .

The crystal data are: C<sub>18</sub>H<sub>18</sub>NOBr; M.W. 344.254; space group  $P2_1/c$ ;  $a=11.985$  (6),  $b=18.765$  (11),  $c=7.260$  (6) Å,  $\beta=94.6$  (1)°,  $Z=4$ ,  $V=1611.2$  Å<sup>3</sup>,  $\rho_c=1.42$ ,  $\rho_o=1.40$  g cm<sup>-3</sup>,  $\mu=33.4$  cm<sup>-1</sup>.

Intensities were collected on the Picker diffractometer with Zr-filtered Mo  $K\alpha$  radiation. The mode was  $\theta$ - $2\theta$  scan, the scan speed was 2°/min over angles of 2°. Stationary-crystal and counter background counts of 20 sec were taken at each end of the scan. The measurements were made up to  $2\theta=55^\circ$ . The reflexions 560,

\* The same nomenclature used for cyclohexane was adopted, where *cis-trans* refers to the configuration of substituents on 5 and 6 [i.e. C(2) and C(3)], while *syn-anti* refers to substituents on 4 and 5 [i.e. C(1) and C(2)].

560, and 560 were taken as standards and monitored after every 50 measurements. They showed good stability during the whole collection. 3677 reflexions were examined, and 1651 with an intensity (corrected for back-

ground) > 3σ were considered observed. Lorentz-polarization and absorption corrections were made by means of the program PICKER, written by R. Scordamaglia. The latter correction was based on the

Table 1. Observed and calculated structure factors

Table with 10 columns: h, k, l, Fo, Fc, h, k, l, Fo, Fc. It contains a large grid of numerical data representing observed and calculated structure factors for various reflections.

Table 1 (cont.)

M K L			FO FF			M K L			FO FF			M K L			FO FF			M K L			FO FF			M K L			FO FF			M K L			FO FF																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						
-3	14	0	271	-132	-2	1	122	-118	6	7	2	361	-261	-1	13	7	2	45	-150	-12	8	1	1	110	191	-10	5	4	5	65	54	-1	6	5	5	76	-90	-4	1	7	4	43	47	-4	1	7	4	75	-17	-1	1	7	4	86	-79	-1	1	7	4	97	-164	-1	1	7	4	108	-113	-1	1	7	4	119	-66	-2	1	7	4	130	-19	-4	1	7	4	141	-113	-4	1	7	4	152	-66	-2	1	7	4	163	-19	-4	1	7	4	174	-66	-2	1	7	4	185	-19	-4	1	7	4	196	-66	-2	1	7	4	207	-19	-4	1	7	4	218	-66	-2	1	7	4	229	-19	-4	1	7	4	240	-66	-2	1	7	4	251	-19	-4	1	7	4	262	-66	-2	1	7	4	273	-19	-4	1	7	4	284	-66	-2	1	7	4	295	-19	-4	1	7	4	306	-66	-2	1	7	4	317	-19	-4	1	7	4	328	-66	-2	1	7	4	339	-19	-4	1	7	4	350	-66	-2	1	7	4	361	-19	-4	1	7	4	372	-66	-2	1	7	4	383	-19	-4	1	7	4	394	-66	-2	1	7	4	405	-19	-4	1	7	4	416	-66	-2	1	7	4	427	-19	-4	1	7	4	438	-66	-2	1	7	4	449	-19	-4	1	7	4	460	-66	-2	1	7	4	471	-19	-4	1	7	4	482	-66	-2	1	7	4	493	-19	-4	1	7	4	504	-66	-2	1	7	4	515	-19	-4	1	7	4	526	-66	-2	1	7	4	537	-19	-4	1	7	4	548	-66	-2	1	7	4	559	-19	-4	1	7	4	570	-66	-2	1	7	4	581	-19	-4	1	7	4	592	-66	-2	1	7	4	603	-19	-4	1	7	4	614	-66	-2	1	7	4	625	-19	-4	1	7	4	636	-66	-2	1	7	4	647	-19	-4	1	7	4	658	-66	-2	1	7	4	669	-19	-4	1	7	4	680	-66	-2	1	7	4	691	-19	-4	1	7	4	702	-66	-2	1	7	4	713	-19	-4	1	7	4	724	-66	-2	1	7	4	735	-19	-4	1	7	4	746	-66	-2	1	7	4	757	-19	-4	1	7	4	768	-66	-2	1	7	4	779	-19	-4	1	7	4	790	-66	-2	1	7	4	801	-19	-4	1	7	4	812	-66	-2	1	7	4	823	-19	-4	1	7	4	834	-66	-2	1	7	4	845	-19	-4	1	7	4	856	-66	-2	1	7	4	867	-19	-4	1	7	4	878	-66	-2	1	7	4	889	-19	-4	1	7	4	900	-66	-2	1	7	4	911	-19	-4	1	7	4	922	-66	-2	1	7	4	933	-19	-4	1	7	4	944	-66	-2	1	7	4	955	-19	-4	1	7	4	966	-66	-2	1	7	4	977	-19	-4	1	7	4	988	-66	-2	1	7	4	999	-19	-4	1	7	4	1010	-66	-2	1	7	4	1021	-19	-4	1	7	4	1032	-66	-2	1	7	4	1043	-19	-4	1	7	4	1054	-66	-2	1	7	4	1065	-19	-4	1	7	4	1076	-66	-2	1	7	4	1087	-19	-4	1	7	4	1098	-66	-2	1	7	4	1109	-19	-4	1	7	4	1120	-66	-2	1	7	4	1131	-19	-4	1	7	4	1142	-66	-2	1	7	4	1153	-19	-4	1	7	4	1164	-66	-2	1	7	4	1175	-19	-4	1	7	4	1186	-66	-2	1	7	4	1197	-19	-4	1	7	4	1208	-66	-2	1	7	4	1219	-19	-4	1	7	4	1230	-66	-2	1	7	4	1241	-19	-4	1	7	4	1252	-66	-2	1	7	4	1263	-19	-4	1	7	4	1274	-66	-2	1	7	4	1285	-19	-4	1	7	4	1296	-66	-2	1	7	4	1307	-19	-4	1	7	4	1318	-66	-2	1	7	4	1329	-19	-4	1	7	4	1340	-66	-2	1	7	4	1351	-19	-4	1	7	4	1362	-66	-2	1	7	4	1373	-19	-4	1	7	4	1384	-66	-2	1	7	4	1395	-19	-4	1	7	4	1406	-66	-2	1	7	4	1417	-19	-4	1	7	4	1428	-66	-2	1	7	4	1439	-19	-4	1	7	4	1450	-66	-2	1	7	4	1461	-19	-4	1	7	4	1472	-66	-2	1	7	4	1483	-19	-4	1	7	4	1494	-66	-2	1	7	4	1505	-19	-4	1	7	4	1516	-66	-2	1	7	4	1527	-19	-4	1	7	4	1538	-66	-2	1	7	4	1549	-19	-4	1	7	4	1560	-66	-2	1	7	4	1571	-19	-4	1	7	4	1582	-66	-2	1	7	4	1593	-19	-4	1	7	4	1604	-66	-2	1	7	4	1615	-19	-4	1	7	4	1626	-66	-2	1	7	4	1637	-19	-4	1	7	4	1648	-66	-2	1	7	4	1659	-19	-4	1	7	4	1670	-66	-2	1	7	4	1681	-19	-4	1	7	4	1692	-66	-2	1	7	4	1703	-19	-4	1	7	4	1714	-66	-2	1	7	4	1725	-19	-4	1	7	4	1736	-66	-2	1	7	4	1747	-19	-4	1	7	4	1758	-66	-2	1	7	4	1769	-19	-4	1	7	4	1780	-66	-2	1	7	4	1791	-19	-4	1	7	4	1802	-66	-2	1	7	4	1813	-19	-4	1	7	4	1824	-66	-2	1	7	4	1835	-19	-4	1	7	4	1846	-66	-2	1	7	4	1857	-19	-4	1	7	4	1868	-66	-2	1	7	4	1879	-19	-4	1	7	4	1890	-66	-2	1	7	4	1901	-19	-4	1	7	4	1912	-66	-2	1	7	4	1923	-19	-4	1	7	4	1934	-66	-2	1	7	4	1945	-19	-4	1	7	4	1956	-66	-2	1	7	4	1967	-19	-4	1	7	4	1978	-66	-2	1	7	4	1989	-19	-4	1	7	4	2000	-66	-2	1	7	4	2011	-19	-4	1	7	4	2022	-66	-2	1	7	4	2033	-19	-4	1	7	4	2044	-66	-2	1	7	4	2055	-19	-4	1	7	4	2066	-66	-2	1	7	4	2077	-19	-4	1	7	4	2088	-66	-2	1	7	4	2099	-19	-4	1	7	4	2110	-66	-2	1	7	4	2121	-19	-4	1	7	4	2132	-66	-2	1	7	4	2143	-19	-4	1	7	4	2154	-66	-2	1	7	4	2165	-19	-4	1	7	4	2176	-66	-2	1	7	4	2187	-19	-4	1	7	4	2198	-66	-2	1	7	4	2209	-19	-4	1	7	4	2220	-66	-2	1	7	4	2231	-19	-4	1	7	4	2242	-66	-2	1	7	4	2253	-19	-4	1	7	4	2264	-66	-2	1	7	4	2275	-19	-4	1	7	4	2286	-66	-2	1	7	4	2297	-19	-4	1	7	4	2308	-66	-2	1	7	4	2319	-19	-4	1	7	4	2330	-66	-2	1	7	4	2341	-19	-4	1	7	4	2352	-66	-2	1	7	4	2363	-19	-4	1	7	4	2374	-66	-2	1	7	4	2385	-19	-4	1	7	4	2396	-66	-2	1	7	4	2407	-19	-4	1	7	4	2418	-66	-2	1	7	4	2429	-19	-4	1	7	4	2440	-66	-2	1	7	4	2451	-19	-4	1	7	4	2462	-66	-2	1	7	4	2473	-19	-4	1	7	4	2484	-66	-2	1	7	4	2495	-19	-4	1	7	4	2506	-66	-2	1	7	4	2517	-19	-4	1	7	4	2528	-66	-2	1	7	4	2539	-19	-4	1	7	4	2550	-66	-2	1	7	4	2561	-19	-4	1	7	4	2572	-66	-2	1	7	4	2583	-19	-4	1	7	4	2594	-66	-2	1	7	4	2605	-19	-4	1	7	4	2616	-66	-2	1	7	4	2627	-19	-4	1	7	4	2638	-66	-2	1	7	4	2649	-19	-4	1	7	4	2660	-66	-2	1	7	4	2671	-19	-4	1	7	4	2682	-66	-2	1	7	4	2693	-19	-4	1	7	4	2704	-66	-2	1	7	4	2715	-19	-4	1	7	4	2726	-66	-2	1	7	4	2737	-19	-4	1	7	4	2748	-66	-2	1	7	4	2759	-19	-4	1	7	4	2770	-66	-2	1	7	4	2781	-19	-4	1	7	4	2792	-66	-2	1	7	4	2803	-19	-4	1	7	4	2814	-66	-2	1	7	4	2825	-19	-4	1	7	4	2836	-66	-2	1	7	4	2847	-19	-4	1	7	4	2858	-66	-2	1	7	4	2869	-19	-4	1	7	4	2880	-66	-2	1	7	4	2891	-19	-4	1	7	4	2902	-66	-2	1	7	4	2913	-19	-4	1	7	4	2924	-66	-2	1	7	4	2935	-19	-4	1	7	4	2946	-66	-2	1	7	4	2957	-19	-4	1	7	4	2968	-66	-2	1	7	4	2979	-19	-4	1	7	4	2990	-66	-2	1	7	4	3001	-19	-4	1	7	4	3012	-66	-2	1	7	4	3023	-19	-4	1	7	4	3034	-66	-2	1	7	4	3045	-19	-4	1	7	4	3056	-66	-2	1	7	4	3067	-19	-4	1	7	4	3078	-66	-2	1	7	4	3089	-19	-4	1	7	4	3100	-66	-2	1	7	4	3111	-19	-4	1	7	4	3122	-66	-2	1	7	4	3133	-19	-4	1	7	4	3144	-66	-2	1	7	4	3155	-19	-4	1	7	4	3166	-66</

weighting scheme suggested by Cruickshank (1965),  $1/w = A + BF_o + CF_o^2$ , where  $A = 38.0$ ,  $B = 1.0$ ,  $C = 0.00316$ . A weight of 0.001 was given to unobserved reflexions. Five isotropic least-squares cycles lowered  $R$  to 0.136. Three cycles carried out after making the Br atom anisotropic gave an  $R$  of 0.109. The following cycles, with all atoms anisotropic, were made with a block-matrix refinement, because of the high number

of parameters involved. Convergence was reached when the  $R$  value was 0.083.

All the hydrogen atoms were revealed by a Fourier difference synthesis, in positions very close to those expected. Their introduction in further least-squares cycles gave a final  $R$  of 0.062. Table 1 lists observed and calculated structure factors. For brevity, unobserved structure factors are omitted. The positional and thermal parameters of non-hydrogen atoms with their standard deviations are given in Table 2; the parameters of the hydrogen atoms are presented in Table 3.

Table 3. Final positional ( $\times 10^3$ ) and thermal ( $\times 10$ ) parameters of hydrogen atoms

	$x/a$	$y/b$	$z/c$	$B$
H(21)	327 (8)	79 (5)	539 (13)	39 (23)
H(31)	519 (8)	93 (5)	460 (12)	39 (21)
H(51)	416 (9)	227 (5)	65 (14)	31 (24)
H(61)	242 (7)	228 (4)	128 (11)	19 (19)
H(22)	897 (8)	15 (5)	534 (14)	26 (24)
H(32)	13 (9)	8 (6)	772 (15)	49 (26)
H(42)	53 (7)	116 (5)	-8 (12)	22 (19)
H(52)	932 (8)	220 (5)	890 (13)	45 (24)
H(62)	785 (10)	224 (6)	658 (16)	44 (32)
H(1)	607 (9)	220 (6)	166 (13)	31 (26)
H(2)	718 (8)	130 (5)	34 (13)	29 (22)
H(3)	593 (8)	34 (5)	188 (13)	25 (22)
H(5A)	588 (9)	87 (6)	-203 (15)	44 (28)
H(5B)	494 (8)	92 (5)	-93 (12)	28 (21)
H(5C)	551 (10)	166 (6)	-197 (16)	57 (30)
H(6A)	790 (7)	9 (4)	-12 (12)	13 (19)
H(6B)	730 (9)	-46 (5)	116 (14)	44 (25)
H(6C)	668 (10)	-28 (6)	-78 (16)	62 (29)

### Discussion of the structure

Bond lengths and angles are given in Fig. 1. Standard deviations are 0.008 Å for the Br-C bond, 0.010–0.012 Å and 0.3–0.4° for other bonds and angles not involving hydrogen atoms, 0.09–0.12 Å and 4–8° for bonds and angles involving hydrogen atoms. For clarity, the following angles are omitted: C(41)-C(1)-N: 110.1; C(1)-C(2)-C(3): 109.4; C(2)-C(3)-C(6): 114.6; H(1)-C(1)-C(2): 118; H(2)-C(2)-C(5): 111; H(3)-C(3)-O: 111; C(2)-C(5)-H(5B): 110; H(5)-C(5)-H(5C): 104; C(3)-C(6)-H(6B): 100; H(6)-C(6)-H(6C): 110°.

The Br-C(11) bond length of 1.915 Å is a little longer than the value of 1.85 Å given by Sutton (1965), but a survey of recent literature shows that this situation is

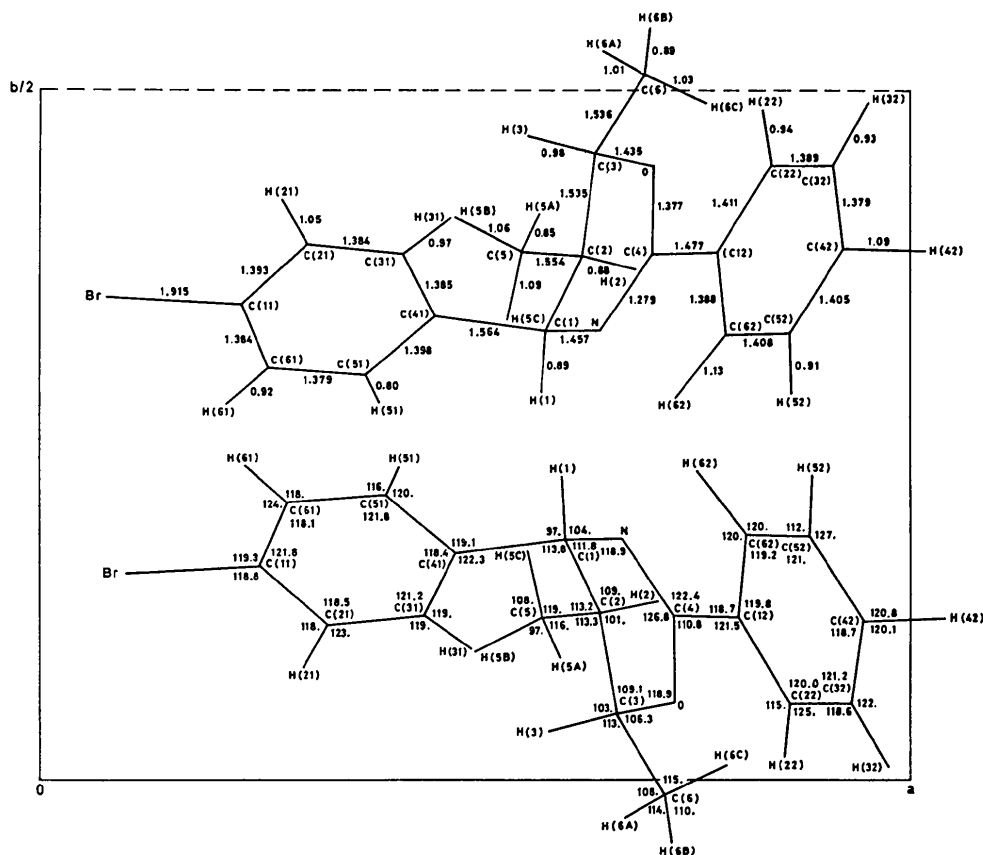
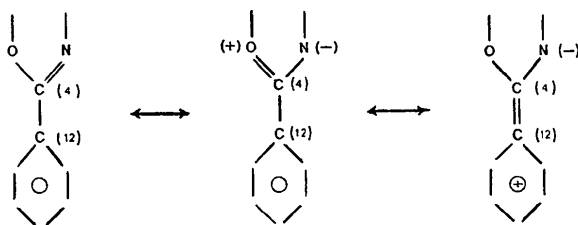


Fig. 1. Projection of the half-cell content on the  $ab$  plane. Atomic numbering, bond distances (Å) and angles (°) are shown.

very common in *p*-bromophenyl groups. Phenyl rings, indicated in the following as PhI and PhII, have geometrical features in good agreement with those usually accepted, with mean bond lengths of 1.387 and 1.396 Å respectively. C<sub>sp3</sub>-C<sub>sp3</sub> bond distances vary from 1.524 to 1.554 Å, with an average of 1.537 Å, in agreement with the standard bond length of 1.526 ± 0.002 Å quoted by Lide (1962). The two C<sub>sp3</sub>-C<sub>sp2</sub> bond distances differ significantly from the standard value of 1.501 ± 0.004 Å (Lide, 1962). The shorter value of 1.477 Å for the C(4)-C(12) bond can be explained by the adjacent double bond, while the longer value of 1.564 Å for C(41)-C(1) is common when a phenyl ring is an axial substituent of a cyclohexane: it can be compared with a similar bond (1.58 Å) in 1-bromo-1-benzoyl-2-phenylcyclohexane (Ducruix & Pascard-Billy, 1972).

The C(3)-O bond has a normal length of 1.435 Å (Lide, 1962), while C(4)-O is shortened by the proximity of the double bond to 1.377 Å (Hall & Ahmed, 1968). The N<sub>sp2</sub>-C<sub>sp3</sub> bond has a value of 1.457 Å, to be compared with 1.472 ± 0.008 (Lide, 1962), while the N=C double bond is lengthened to 1.279 Å compared with the generally accepted value of 1.24 Å (*International Tables for X-ray Crystallography*, 1962). This fact, with the shortness of single bonds involving C(4), clearly indicates a partial delocalization of the double bond, with conjugation between the PhII and oxazine rings:



The C-H bonds vary from 0.80 to 1.13 Å, with a mean value of 0.97 Å. Equations of the mean-square planes of the molecule and deviations of the atoms from them are listed in Table 4. The phenyl rings are planar to a good approximation. The deviation from the PhI plane appears significant for the Br atom (+0.057 Å). Good planarity was also found for five of the six atoms of the oxazine ring, only C(2) being significantly out of plane (-0.632 Å). The small dihedral angle of 1.5° between PhII and the heterocyclic ring and the low value of the mean-square distance ( $\Delta_{ms}$ ) obtained including the atoms of both rings in the calculation suggests that all this portion of the molecule is substantially planar. Between the oxazine and PhI rings however there is an angle of 84.5°. Newman projections along some C-C bonds are shown in Fig. 2(a).

Methyl groups C(5) and C(6) are both equatorial, in a *trans* configuration. The PhI ring assumes an axial position and is *syn* with respect to the C(5) methyl group. These results are in good agreement with those obtained from n.m.r. spectra (Giordano & Abis, 1972).

Partially saturated six-atom rings generally have a

conformation intermediate between planar phenyl-type and chair cyclohexane-type. Cyclohexene is a good example of this situation, with four atoms planar and the remaining two over and under the ring plane. This conformation, called 'half-chair', is also common in heterocyclic rings (Konnert, Karle & Karle, 1970; Rohrer & Sundaralingam, 1970).

As shown in Fig. 2(b), in the oxazine ring examined by us five atoms are approximately planar and one is out of the plane. A similar conformation can be found in barbituric-type rings (Pascard-Billy, 1970) and can be called 'half-boat'. The planarity of the five atoms can be correlated with the conjugation of the heterocyclic ring with PhII, and by the tendency of the axial PhI to become equatorial, thus applying a strain to the oxazine ring. Another consequence of the conjugation between the two rings is the coplanarity of the PhII

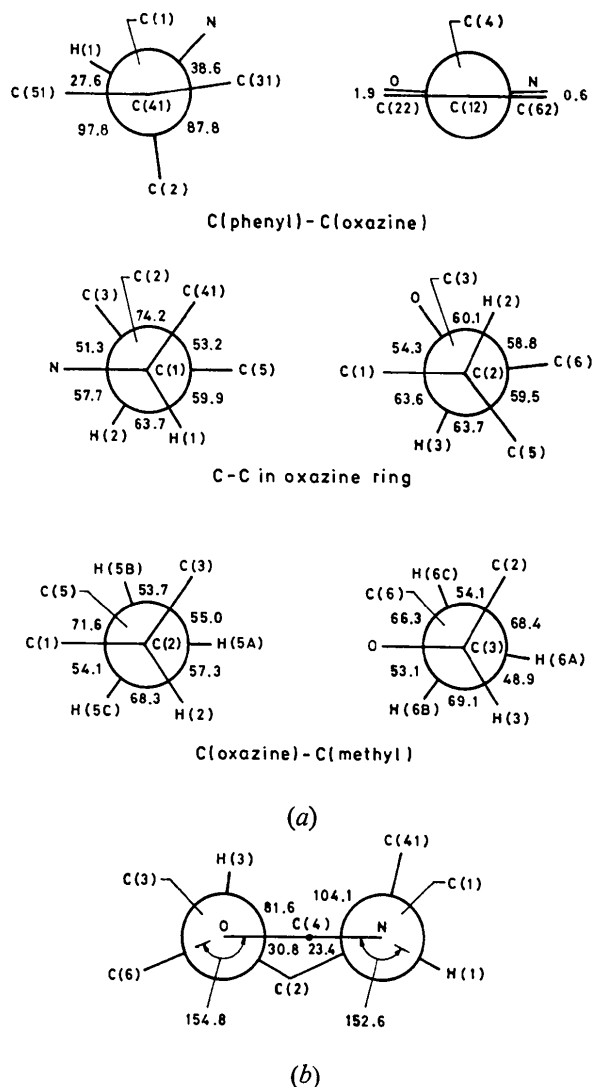


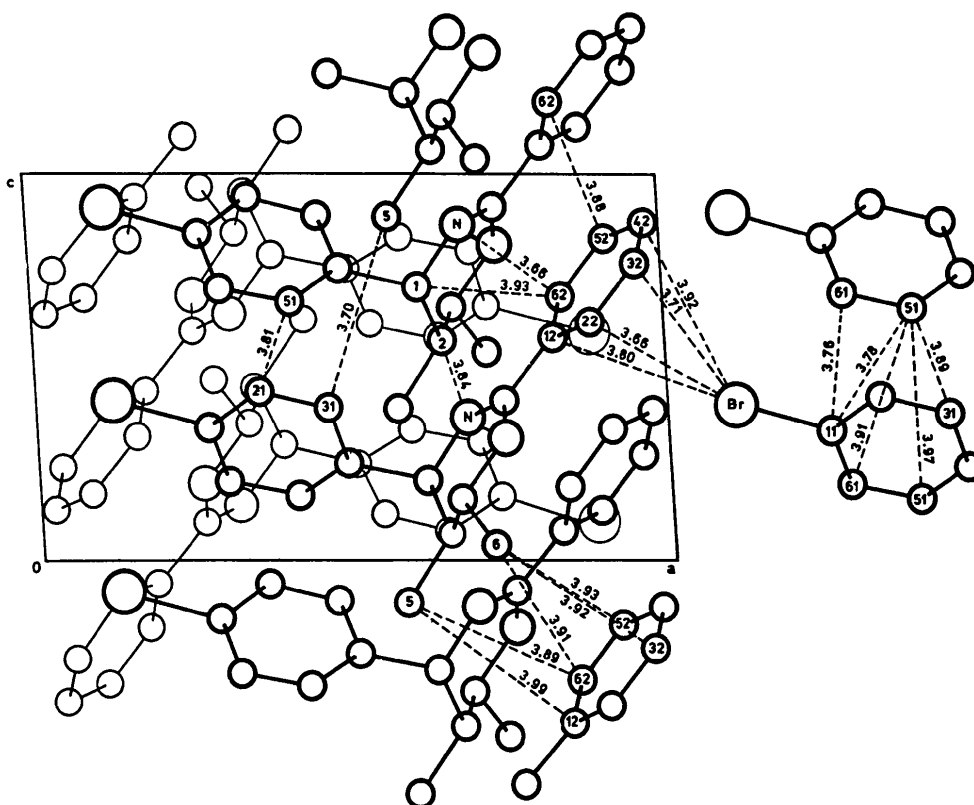
Fig. 2. (a) Relevant Newman projections of carbon-carbon bonds. (b) Schematic view of the oxazine ring along its mean-square plane.

Table 4. *Least-squares planes and deviations*Coefficients of the plane equations  $Ax + By + Cz - D = 0$  are referred to crystallographic axes.

	PhI ring		PhII ring	Oxazine ring	
<i>A</i>	0.104	0.110	-0.750	-0.722	-0.757
<i>B</i>	0.722	0.722	-0.321	-0.321	-0.322
<i>C</i>	0.674	0.672	0.636	0.609	0.626
<i>D</i>	4.035	4.079	-5.517	-5.805	-5.649
Br	0.057 Å	0.048* Å			
C(11)	0.001*	-0.022*			
C(21)	-0.009*	-0.027*			
C(31)	0.019*	0.007*			
C(41)	0.020*	-0.023*			
C(51)	0.013*	0.006*			
C(61)	-0.003*	-0.027*			
C(1)	0.014	0.038*		-0.022* Å	-0.048* Å
C(2)				-0.632	
C(3)				0.021*	0.002*
C(4)				-0.003*	0.022*
N				0.025*	0.035*
O				-0.021*	-0.010*
C(12)			0.001* Å		0.013*
C(22)			0.008*		0.017*
C(32)			-0.006*		-0.014*
C(42)			-0.003*		-0.020*
C(52)			0.010*		-0.003*
C(62)			0.008*		0.007*
4 ms†	0.019	0.036	0.010	0.032	0.025

\* Atoms included in calculations of least-squares planes.

† Mean square distance.

Fig. 3. Molecular packing seen along the *b* axis. Intermolecular distances shorter than 4.00 Å are indicated.

and oxazine rings, though this conformation along C(4)–C(21) should be sterically unfavourable. In fact, the oxygen atom is at a minimum possible distances from C(22) (2.704 Å) and H(22) (2.30 Å). These values are a little smaller than the normal intramolecular distances listed by Haschemeyer & Rich (1967). Other short intramolecular distances are N–H(62) (2.30 Å) and O–H(6C) (2.36 Å).

The oxazine molecules are packed three-dimensionally with van der Waals contacts, the shortest intramolecular distances being 3.66 Å between Br and C(22) and between N and C(62) of two neighbour molecules. Intermolecular distances less than 4.00 Å are showed in Fig. 3.

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#### References

- ABIS, L. & GIORDANO, C. (1973). *J. Chem. Soc. Perkin I*. In the press.
- CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*, chapter 14. Edited by J. S. ROLLETT. London: Pergamon Press.
- DUCRUIX, A. & PASCARD-BILLY, C. (1972). *Acta Cryst.* **B28**, 1848–1852.
- GIORDANO, C. & ABIS, L. (1973). *Gazz. Chim. Ital.* To be published.
- GIORDANO, C., RIBALDONE, G. & BORSOTTI, G. (1971). *Synthesis*, 92–95.
- HALL, S. R. & AHMED, F. R. (1968). *Acta Cryst.* **B24**, 346–355.
- HASCHEMEYER, A. E. V. & RICH, A. (1967). *J. Mol. Biol.* **27**, 369–384.
- IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743–748.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KONNERT, J., KARLE, I. L. & KARLE, J. (1970). *Acta Cryst.* **B26**, 770–778.
- LIDE, D. R. (1962). *Tetrahedron*, **17**, 125–134.
- MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.
- PASCARD-BILLY, C. (1970). *Acta Cryst.* **B26**, 1418–1425.
- ROHRER, D. C. & SUNDARALINGAM, M. (1970). *Acta Cryst.* **B26**, 546–553.
- SCHMIDT, R. R. (1968). *Tetrahedron Lett.* pp. 3443–3446.
- SCHMIDT, R. R. (1970). *Chem. Ber.* **103**, 3242–3251.
- SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. London: The Chemical Society.

*Acta Cryst.* (1973). **B29**, 1196

## The Influence of Substituents on the Equilibrium Bisorcaradiene $\rightleftharpoons$ [10]Annulene. The Crystal and Molecular Structure of 11,11-Dimethyltricyclo[4,4,1,0<sup>1,6</sup>]undeca-2,4,7,9-tetraene

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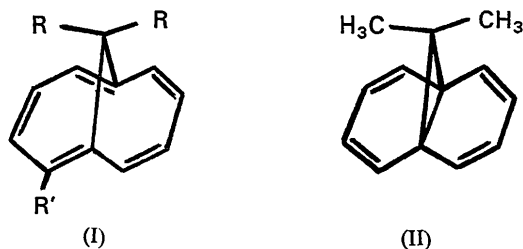
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Crystals of 11,11-dimethyltricyclo[4,4,1,0<sup>1,6</sup>]undeca-2,4,7,9-tetraene are triclinic,  $a = 8.089$ ,  $b = 7.007$ ,  $c = 9.886$  Å,  $\alpha = 100.47^\circ$ ,  $\beta = 95.91^\circ$ ,  $\gamma = 115.45^\circ$ , space group  $P1$ , with two molecules in the asymmetric unit. These are approximately related by partial operators of symmetry (twofold screw axes  $2_p$  with  $|p| < 1$ ). The molecules show  $mm2$  ( $C_{2v}$ ) symmetry with a bisorcaradiene configuration. The central bond lengths in the two molecules are 1.836 and 1.780 Å ( $\sigma = 0.007$  Å) for libration-corrected coordinates. *Ab initio* molecular orbital calculations are in agreement with considerations on the molecular geometry in confirming the presence of a long bond which closes the cyclopropane ring.

### Introduction

As part of a programme of study on the molecular geometry of systems with  $4n + 2$   $\pi$ -electrons ( $n$  greater than 1) (Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972; Gramaccioli, Mugnoli, Pilati, Raimondi & Simonetta, 1972; Gramaccioli & Simonetta, 1971; Gramaccioli, Mimun, Mugnoli & Simonetta, 1971), an interesting problem arose in comparing structural results for two 'similar' types of compounds, (I) and (II), for which chemical and spectroscopic data suggested quite different configurations (Vogel, 1969).



(a) R = H, R' = COOH; (b) R = F, R' = H

The structure determination of 1,6-methano[10]annulene-2-carboxylic acid (Ia) (Dobler & Dunitz, 1965),