Crystal Structure of 1,2-Bis-(4-bromophenyl)-3,5-dimethyl-4-oxo-6,7-diazabicyclo[3,2,0]hept-2-ene-6,7-dicarboxylate

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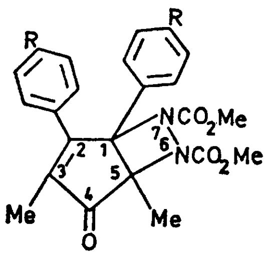
Crystals of the title compound (Ib) are monoclinic with $Z = 4$ in a unit cell of dimensions $a = 12{\cdot}395$ $b = 15{\cdot}527$, $c = 11{\cdot}773$ Å $\beta = 92{\cdot}8°$; space group $P2_1/n$. The structure was solved from diffractometer data by Patterson and Fourier methods and refined to R 0·071 for 1959 independent reflections. Atoms of the four-membered ring are displaced from a least-squares plane by ±0·057 Å. The two planes for the two triangles CNN and CCN intersect at 172·9°. The five-membered ring is planar (maximum displacement 0·023 Å) and is buckled with respect to the four-membered ring the dihedral angle being 112°. The two phenyl rings are tilted at angles of 58·4 and 86·2° with respect to the five-membered ring. The mean planes of the two phenyl rings intersect at 66·4°. The two Br–C(Ph) distances are 1·893(13) and 1·940(12) Å. Interatomic distances in the four-membered ring are: C–C 1·582(17) C–N 1·550(14) and 1·529(15) and N–N 1·467(14) Å. Bond distances for the ester groups at position 6 and 7 are: N–C 1·432(17) and 1·386(18) C=O 1·160(16) and 1·186(19) C–O 1·375 and 1·350 and O–C(Me) 1·511(17) and 1·452(18) Å.

DURING a general study of the reactions of azodicarbonyl compounds with cyclic dienes [1-4] the reaction of 2,5-dimethyl-3,4-diphenylcyclopentadienone with azoesters was examined. Heating under reflux of the diene with dimethyl azodicarboxylate in bromobenzene gave a nearly quantitative yield of the adduct $C_{23}H_{22}N_2O_5$, (Ia),



(I) a; R = H
b; R = Br

The systematic numbering is shown here.

m.p. 200—201 °C. Its chemical properties were those expected for the diazetidine (Ia), but two spectroscopic features were not easily reconcilable with such a structure. The ^{1}H n.m.r. spectrum showed an unusually high-field absorption for one of the ester methyl groups, at τ 7·05 in deuteriochloroform. Furthermore the high-resolution mass spectrum showed a peak at M^+ 275·1546, due to the ion $C_{19}H_{19}N_2^+$ (calc. value 275·1558); this peak clearly contained one of the ester methyl groups which must therefore have been bonded either to nitrogen or to carbon in the ion. Current work on the mass spectra of adducts of this type and related compounds suggests that alkyl group migration from oxygen to nitrogen is a general process in diurethanes. Details will be published elsewhere.

In view of these anomalies an independent confirmation of the diazetidine structure was required. Accordingly, the related compound $C_{23}H_{20}Br_2N_2O_5$, (Ib), m.p. 198—199 °C was synthesized from the *p,p'*-dibromocyclopentadienone and dimethyl azodicarboxylate. It too showed a high-field methyl adsorption in its ^{1}H n.m.r. spectrum, at τ 7·0, and a peak at M^+ 432·9728, due to the ion $C_{19}H_{17}{}^{79}Br^{81}BrN_2^+$ (calc. 432·9738), in its mass spectrum. The X-ray crystal structure analysis of the dibromo-derivative was undertaken and revealed the configuration as (Ib). In view of the similarity in chemical properties and spectroscopic observations, it thus clearly indicates that (Ib) is the *p,p'*-dibromo-derivative of (Ia).

A literature study revealed the X-ray analysis of only one diazetidine derivative, the α-1-(*p*-bromophenyl)-phenylmethylene-3-oxo-1,2-diazetidinium inner salt, which has interesting structural features but is atypical in that the four-membered ring is dipolar and completely planar.[5]

EXPERIMENTAL

Crystals of the title compound, m.p. 198 °C from methanol, are colourless prisms, slightly elonaged along c with well developed (010) and (100) faces. The cell constants and space group data were derived from rotation, Weissenberg and precession photographs.

Crystal Data.—$C_{23}H_{20}Br_2N_2O_5$, $M = 564{\cdot}24$. Monoclinic, $a = 12{\cdot}395(8)$, $b = 15{\cdot}527(8)$, $c = 11{\cdot}773(8)$ Å, $\beta = 92{\cdot}8$ $(0{\cdot}4)°$, $U = 2262{\cdot}3$ Å^3, $D_m = 1{\cdot}64$, $Z = 4$, $D_c = 1{\cdot}656$, $F(000) = 1128$. Space group: $P2_1/n$ from systematic absences, Cu-k_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-k_α) = 53·6 cm^{-1}.

A crystal measuring 0·2 × 0·3 × 0·4 mm along a, b and c was mounted with [001] along the ϕ axis of the goniostat of a General Electric XRD 6 automatic diffractometer. 2121 reflections with $2\theta \leqslant 100°$ (Cu-K_α) were measured by the θ—2θ scan technique. The scan range was $(1{\cdot}8 + 0{\cdot}6\tan\theta)°$ with a scan speed of 2° min^{-1}.

Four strong reflections were chosen as standards and were measured between each hundred reflections to apply a small correction (<2·5%) for the fluctuation of intensity during the course of data collection. The background was

[1] P. C. Arora and D. Mackay, *Chem. Comm.*, 1969, 677.
[2] D. Mackay, J. A. Campbell, and C. P. R. Jennison, *Canad. J. Chem.*, 1970, **48**, 81.
[3] J. A. Campbell, D. Mackay, and T. D. Sauer, *Canad. J. Chem.*, 1972, **50**, 371.
[4] C. Y.-J. Chung, D. Mackay, and T. D. Sauer, *Canad. J. Chem.*, 1972, **50**, 1568.
[5] C. J. Fritchie, jun., and J. E. Wells, *Chem. Comm.*, 1968, 917.

measured at the beginning and end of each scan. 1959 reflections had $I > 1{\cdot}5\sigma(I)$ and were considered observed (92·4%). Lorentz and polarization factors were applied to derive the structure amplitude.

Determination and Refinement of the Structure.—The two bromine atoms were located from an unsharpened three-dimensional Patterson synthesis. A three-dimensional Fourier map, based on the phase calculated from the bromine atoms, revealed the 28 positions of the 30 non-hydrogen light atoms. Two bromine atoms alone gave R 0·42. Assuming all light atoms as carbon, one cycle of full-matrix least-squares gave R 0·20 and the difference-Fourier synthesis gave the position of the remaining two light atoms. By consideration of (i) the bond distances and angles in the skeleton, (ii) the analytical formula, and (iii) the isotropic thermal parameters it was possible to distinguish nitrogen and oxygen from carbon atoms. With proper atomic scattering factors and isotropic thermal parameters for each atom, one cycle of least-squares reduced R to 0·13. The difference-Fourier had high electron-density around the location of the two bromine atoms, and anisotropic thermal parameters were introduced for them. The full-matrix least-squares refinement immediately reduced R to 0·081. At this point, the terminal methyl carbon and oxygen atoms were allowed to have anisotropic temperature parameters. One further cycle of least-squares brought R to 0·071 * and the refinement was stopped. The function minimized the $\Sigma(|F_o| - |F_c|)^2$, and an analysis based on ranges of observed structure factors gave little variation of mean $|F_o| - |F_c|$ (Table 1). This suggested that the unit weighting scheme

TABLE 1

Weighting analysis based on ranges of $|F_o|$ and ($\sin\theta/\lambda$)

Range of $\lvert F_o\rvert$	Error *	Range of ($\sin\theta/\lambda$)	Error *
0·0—8·4	3·8	0·0—0·231	6·4
8·4—13·0	3·6	0·231—0 291	4 6
13 0—17·9	2·8	0·291—0·333	3·9
17·9—23·2	2·9	0·333—0·366	2·8
23·2—29·1	3·3	0·366—0·394	2·8
29·1—37·2	3·4	0·394—0·419	2·9
37·2—46·1	4·1	0·419—0·441	3·0
46·1—57·2	3·9	0·441—0·461	3·2
57·2—76·8	4·9	0·461—0·480	3·1
76·8-up	6·9	0·480—0·497	3·0

$$\text{* Error} = \left[\frac{\Sigma(|F_o| - |F_c|)^2 \times n_t}{(n_t - n_v)\cdot n}\right]^{1/2}$$ where n_t, total number of reflections (1959); n_v, number of variables; n, number of reflections in the range.

was satisfactory. The final co-ordinates and thermal parameters are given in Table 2. The aromatic scattering factors of ref. 6 were used for all the atoms, no dispersion corrections being made.

DISCUSSION

The bond lengths and the numbering of the atoms are given in Figure 1(a) and the bond angles in Figure 1(b). The C(11)–Br(1) distance of 1·893(13) is comparable with 1·86(1) [7] found in bromobenzene. The value of 1·940(12) found for C(21)–Br(2) can not be considered to be significantly different since the difference may arise from thermol libration. Chemically, no evidence for the difference has been found. However, C(Ph)–Br distances ranging from 1·88—1·95 Å have been found in a series of compounds.[8]

TABLE 2

Positional (fractional) and thermal (Å^2) parameters,* with standard deviations in parentheses

Atom	x	y	z	B
Br(1)	0·43446(14)	−0·09495(11)	−0·12497(14)	
Br(2)	−0·13056(16)	−0·32963(10)	0·06770(15)	
O(1)	0·0214(9)	0·2406(6)	0·3013(9)	
C(1)	−0·1349(12)	0·1122(9)	0·2098(12)	
C(2)	0·2549(12)	0·1975(9)	0·2650(12)	
C(3)	0·0741(13)	−0·1937(9)	0·4397(13)	
C(4)	0·3936(13)	0·0941(11)	0·6424(12)	
O(A1)	0·1141(8)	−0·0404(6)	0·5384(7)	
O(A2)	0·1325(8)	−0·1226(5)	0·3801(7)	
O(A3)	0·2672(9)	0·2067(6)	0·5221(8)	
O(A4)	0·3182(9)	0·0685(6)	0·5503(9)	
C(11)	0·3614(11)	−0·0480(9)	−0·0015(11)	2·4(3)
C(12)	0·2978(11)	0·0244(8)	−0·0209(11)	2·4(3)
C(13)	0·2355(10)	0·0538(8)	0·0688(11)	2·2(3)
C(14)	0·2393(10)	0·0126(8)	0·1732(10)	1·7(2)
C(15)	0·3070(11)	−0·0574(8)	0·1902(11)	2·4(3)
C(16)	0·3684(11)	−0·0892(9)	0·1030(11)	2·9(3)
C(21)	−0·0762(11)	−0·2177(8)	0·1164(11)	2·3(3)
C(22)	0·0058(11)	−0·1845(9)	0·0573(11)	2·6(3)
C(23)	0·0455(11)	−0·1022(9)	0·0918(11)	2·6(3)
C(24)	0·0002(10)	−0·0588(8)	0·1819(10)	2·2(3)
C(25)	−0·0880(11)	−0·0950(9)	0·2376(11)	2·5(3)
C(26)	−0·1274(11)	−0·1773(9)	0·2029)11)	2·9(3)
C(51)	0·1613(10)	0·0400(8)	0·2560(10)	1·8(3)
C(52)	0·0461(10)	0·0262(8)	0·2238(10)	1·9(3)
C(53)	−0·0177(10)	0·0972(8)	0·2360(10)	2·1(3)
C(54)	0·0532(11)	0·1684(9)	0·2835(11)	2·8(3)
C(55)	0·1661(10)	0·1357(8)	0·3022(10)	2·1(3)
N(1)	0·1953(9)	0·0116(7)	0·3788(8)	2·1(2)
C(A1)	0·1389(11)	−0·0493(9)	0·4454(12)	2·5(3)
N(2)	0·1826(9)	0·0994(7)	0·4224(9)	2·6(2)
C(A2)	0·2601(13)	0·1324(11)	0·4993(12)	3·3(3)

Anisotropic thermal parameters

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Br(1)	72(1)	40(1)	73(2)	7(1)	22(1)	−10(1)
Br(2)	98(2)	27(1)	87(2)	−24(1)	8(1)	−12(1)
O(1)	81(9)	19(5)	117(11)	8(6)	−22(8)	−21(6)
C(1)	47(12)	30(7)	67(13)	2(8)	−9(10)	−3(8)
C(2)	73(13)	22(7)	60(13)	−21(8)	14(11)	8(8)
C(3)	81(14)	24(7)	81(14)	−21(9)	5(12)	11(8)
C(4)	78(14)	64(10)	49(12)	−25(11)	−53(11)	0(9)
O(A1)	82(9)	32(5)	38(8)	−6(5)	26(10)	−1(9)
O(A2)	69(8)	20(4)	50(8)	−8(5)	7(10)	4(9)
O(A3)	106(10)	25(5)	79(10)	−12(6)	−29(8)	−13(6)
O(A4)	73(9)	34(5)	91(11)	−11(6)	−24(8)	−1(6)

* Anisotropic thermal parameters are in the form: $\exp - 10^{-4}[b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl]$.

In the [3,2,0]-bicyclic system, the five-membered ring C(51), C(52), C(53), C(54), C(55), which has three sp^2 hybridized carbon atoms [C(52), C(53), and C(54)] is planar, as might be expected, the maximum displacement from the mean plane being 0·023 Å. The equations of mean planes and interplanar angles are listed in Table 3. The four-membered ring is slightly buckled, with displacements of ±0·057 Å, the angle between the C(51),

* Tables of observed and calculated structure factors are listed in Supplementary Publication No. SUP 20491 (3 pp., 1 microfiche). For details of Supplementary Publications see *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.
[7] *Chem. Soc. Special Publ.*, No. 11, 1958, and No. 18, 1965.
[8] B. Rerat, *Acta Cryst.*, 1969, *B*, 1392.

N(1), N(2) and C(51), C(55), N(2) planes being 172·9°. The four internal angles are all quite close to 90°. The bond angles not constrained by the ring geometry all have values greater than those usually found for tetra-

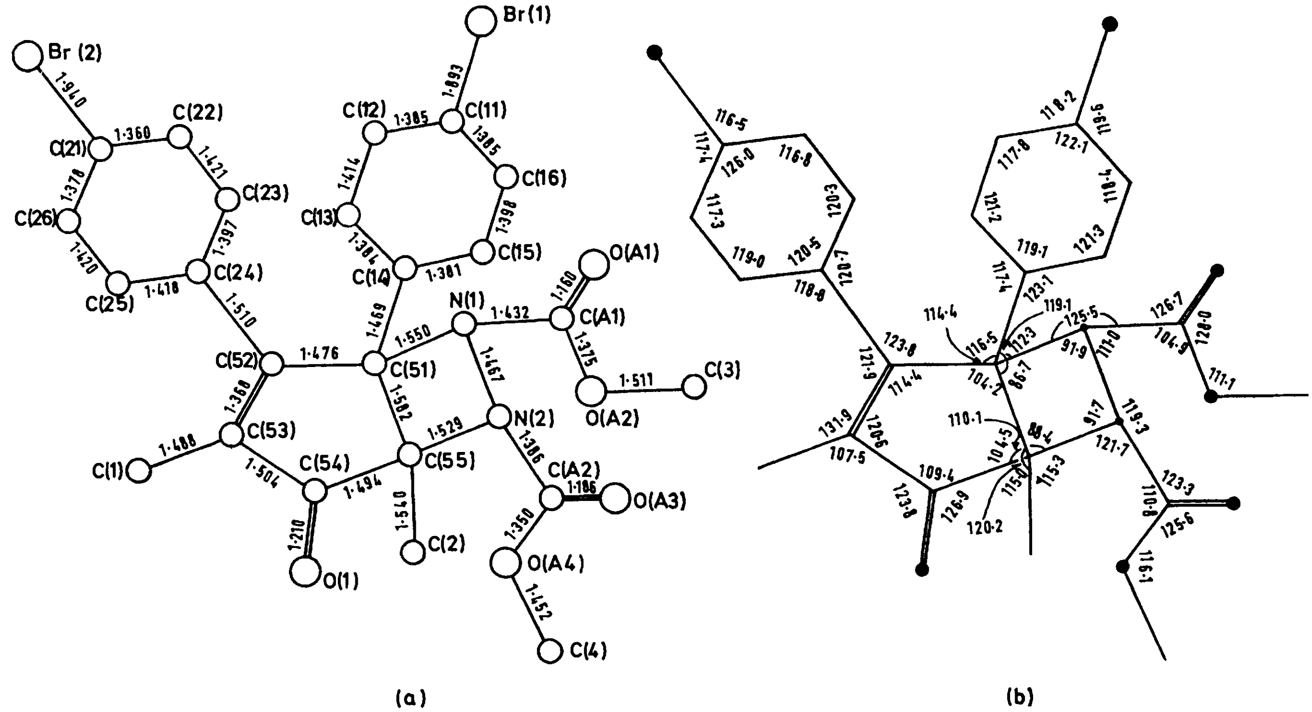


FIGURE 1 (a) The arbitrary crystallographic atom numbering system (used in the text) and bond distances; mean standard deviations: bonds involving Br atoms, 0·013, bonds involving O or N 0·017, and C–C bonds 0·018 Å. (b) Bond angles; mean standard deviation 0·6°

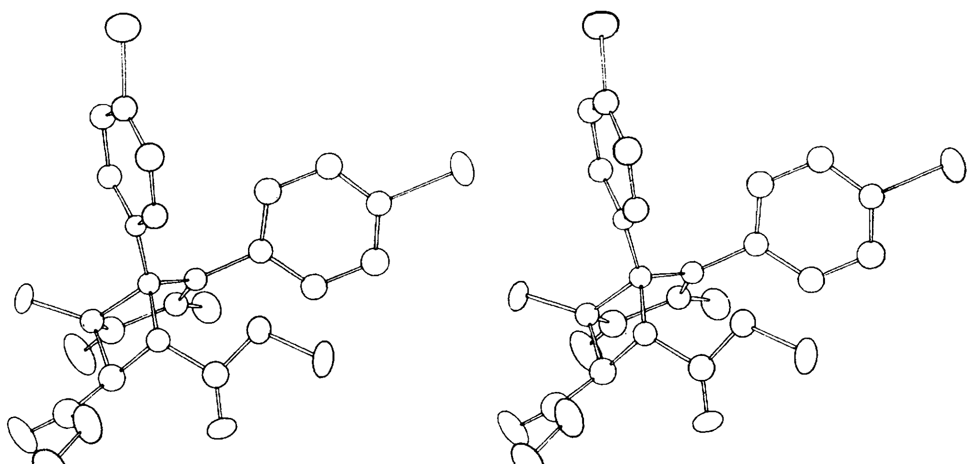


FIGURE 2 A stereoscopic view of the molecule

hedral configurations. This is probably the result of spatial rearrangement of the substituents. The mean plane of the four-membered ring intercepts that of the five-membered ring at an angle of 112·4°.

From the structure of the molecule, it might be thought that the bond C(51)–C(14) should be longer than the bond C(52)–C(24) because C(51) is sp^3 hybridized whereas C(52) is sp^2 hybridized. The converse is in fact found. The distance of 1·469(16) Å for C(51)–C(14) is short compared with similar types of bond lengths of 1·50(1) and 1·52(1) found in tetraphenylmethane [9] and toluene,[7] but it is not significant. The distance of 1·510(17) Å for C(53)–C(24) is also to be expected for a bond linking an olefinic and an aromatic system, where the usual resonance responsible for shortening such a σ bond is com-

[9] P. Chieh, *J.C.S. Dalton*, 1972, 1207.

pletely inhibited here since the phenyl ring at C(52) is rotated out of the plane of the five-membered ring, Table 3, by an angle of 58·4°. The value of 1·476(17) Å for C(51)–C(52) is slightly short (by 3σ), compared with the mean value of 1·53(1) for this type of single bond, C·C:C, found in $Me_2C=CH_2$, MeCH:CHMe, and $Me_2C:CMe_2$.[7] The value of 1·582(17) Å for C(51)–C(55) is longer than the expected value [1·54(1) Å] by 2·5σ; however, it is still within experimental error.

TABLE 3

Equations of mean planes and interplanar angles

(*a*) Equations of mean planes in the form $lX + mY + nZ = P$ where X, Y, and Z are co-ordinates in Å referred to orthogonal axes *a*, *b*, and *c* *

Plane	Atoms	*l*	*m*	*n*	*p*	Max. displacement
(1)	C(11)—(16)	0·7401	0·5979	0·3079	2·897	0·014
(2)	C(21)—(26)	0·6184	−0·4339	0·6552	1·719	0·019
(3)	C(24), C(51)—(53)	−0·2085	−0·2689	0·9404	2·276	0·004
(4)	C(1), C(52)—(54)	−0·2408	−0·2886	0·9267	2·216	0·005
(5)	O(1), C(53)—(55)	−0·2507	−0·2707	0·9295	2·261	0·005
(6)	C(51)—(55)	−0·2303	−0·3025	0·9249	2·193	0·023
(7)	N(1), N(2), C(51), C(55)	0·9861	0·0985	−0·1335	1·539	0·057
(8)	N(1), C(A1) O(A1), O(A2)	0·8700	−0·3227	0·3272	3·509	0·034
(9)	N(2), C(A2), O(A3), O(A4)	−0·6944	−0·0879	0·7142	2·001	0·028

(*b*) Interplanar angles (deg.)

(1)—(6)	86·2	(6)—(7)	112·4
(2)—(6)	58·4	(3)—(4)	2·3
(3)—(6)	2·4	(4)—(5)	1·0
(4)—(6)	1·0	(3)—(5)	2·4
(5)—(6)	2·1	(1)—(2)	66·4

There are some differences between the lengths of corresponding bonds in the two ester groups but only O(A2)–C(3) [1·511(17)] and O(A4)–C(4) [1·452(18) Å] are significantly different (by 3·3σ). The former seems unusually long since the latter is typical of known values in other urethane systems.[10] The stereoscopic diagram (Figure 2) shows that the methyl group, C(3), of the ester group attached to N(1) is close to the bromophenyl group bonded to C(52). The distances from C(3) to atoms of the bromophenyl ring, C(21), C(22)—(26), are 4·17, 4·54, 4·33, 3·76, 3·40, and 3·66 Å. If this particular conformation of the ester group is also a low-energy one in solution then it is clear that its methyl group, on a time-average basis, is very close to the face of the bromophenyl ring. It would thus be magnetically strongly shielded, in agreement with the high chemical shift value observed.

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[10] R. A. Smith, J. E. Baldwin, and L. C. Paul, *J. Chem. Soc.* (*B*), 1967, 112; L. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *J. Amer. Chem. Soc.*, 1968, **90**, 5023; R. Allmann, *Angew. Chem. Internat. Edn.*, 1970, **9**, 958.