Crystal Structure of *NN'*-Bis-*p*-Bromophenyl-2,2,4,4-tetramethylcyclobutane-1,3-di-imine

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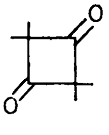
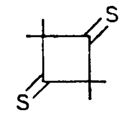
The crystal and molecular structure of the title compound has been determined from three-dimensional *X*-ray diffraction data. Crystals are monoclinic, space group $P2_1/c$, $Z = 2$, with cell dimensions $a = 12.64(1)$, $b = 10.11(1)$, $c = 7.60(1)$ Å, and $\beta = 94.42(9)°$. Data were collected on a diffractometer, and the structure was solved by normal heavy-atom methods and refined by block-matrix least-squares analysis to *R* 0.064. The molecule contains an inversion centre with a planar cyclobutane ring. The ring bond parameters are: C–C(ring) 1.52(1), C–CH_3 1.55(1), and C–N 1.26(1) Å. The bond angles in the ring are 86.1(9) and 93.9(9)°.

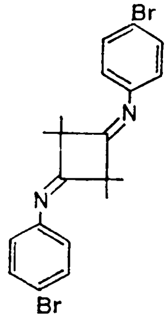
In recent years the crystal structures of 2,2,4,4-tetramethylcyclobutane-1,3-dione [1] (I) and the corresponding dithione [2] (II) have been reported. We now report the crystal structure of the title compound (III) which offers an excellent example to make a comparison of the effects of carbon π bonded to oxygen, sulphur, and nitrogen in structurally similar environments. Previous work has indicated the importance of the 1,3-transannular distance and its effect on the optical absorption spectra of (I) and (II). The possible interaction of the *p* orbitals on the 1,3-transannular carbons was suggested to be a function of the 1,3-bond distance. Since the dione (I) shows two $n \rightarrow \pi^*$ transitions while the dithione (II) shows only one, it would be expected that the distance between transannular carbons would be different. This however is not observed. Compounds of general structure (III), in which the groups attached to the nitrogen are transparent in the u.v. region, show two $n \rightarrow \pi^*$ transitions.[3] The crystal structure of (III) was undertaken to ascertain any 1,3-π-interaction and to elucidate any possible differences relative to the dione (I) and dithione (II).



(I)



(II)



(III)

EXPERIMENTAL

A sample of (III) was prepared by reaction of tetramethylcyclobutane-1,3-dione with an excess of *p*-bromoaniline in toluene. The mixture was heated under reflux for 10 h with toluene-*p*-sulphonic acid present as a catalyst. Water was removed as it formed by use of a Dean–Stark trap. The product was obtained from the cooled toluene solution.

The crystals used for the *X*-ray diffraction work were obtained by slow cooling of an ethanol solution. Elemental analysis, mass spectral data, i.r., and n.m.r. data were all consistent with structure (III).

The approximate cell dimensions of the crystal as well as its alignment on the diffractometer were determined by the technique of ref. 4. The crystal was rod-shaped with dimensions *ca.* 0.1 × 0.1 × 0.3 mm. By use of graphite-monochromated reflections, 11 high-angle reflections were centred at 2θ and at -2θ and accurate lattice constants determined with local programs.

Crystal Data.—$C_{20}H_{20}Br_2N_2$, $M = 448.2$. Monoclinic, $a = 12.64(1)$, $b = 10.11(1)$, $c = 7.60(1)$ Å, $\beta = 94.42(9)°$, $U = 968.3$ Å^3, $D_m = 1.49$, $Z = 2$, $D_c = 1.53$ g cm^{-3}, $\mu = 44.5$ cm^{-1} for Mo-K_α radiation, $\lambda = 0.7107$ Å. Space group $P2_1/c$.

Integrated intensities corrected for background were measured for one quarter of the reciprocal sphere out to 2θ 40°. Standard deviations were obtained from counter statistics: $\sigma_I^2 = C_T + C_B + (0.03\ C_T)^2 + (0.03\ C_B)^2$ where C_T and C_B represent the total background counts, respectively, and the factor 0.03 represents an estimate of nonstatistical errors. The 723 reflections with $I > 2\sigma_I$ were considered observed and used in the refinement. No absorption correction or dispersion correction was deemed necessary.

The positions of the bromine atoms were located from a Patterson synthesis and used for initial phasing. The rest of the molecule was located in a straightforward manner by conventional Fourier techniques. In the block-matrix least-squares refinement procedure used, half the parameters were fixed while the other half were allowed to vary, because of computer time limitations. Non-hydrogen atomic scattering factors were taken from ref. 5. Hydrogen atoms, located on a difference Fourier map, were included in least-squares refinements but with isotropic thermal parameters corresponding to the carbon atoms to which they are attached. All other atoms were refined anisotropically. A weighting scheme based on counter statistics [6] was applied,

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[1] de M. C. Riche and M. M. M. Janat, *Compt. rend.*, 1972, **275**, 543.

[2] C. D. Shirrell and D. E. Williams, *Acta Cryst.*, 1973, **B29**, 1648.

[3] E. A. Schmidt, J. J. Worman, W. P. Jensen, R. Schultz, and E. S. Olson, *Spectrochim. Acta*, in the press.

[4] R. A. Jacobson, 'An Algorithm for Automatic Indexing and Bravais Lattice Selection. The Programs BLIND and ALICE,' U.S. Atomic Energy Commission Report IS 3469, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1974.

[5] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[6] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, New York, 1968.

with individual weight factors: $w_i = (\sigma_{F_i})^{-2}$. The final R was 0.064 for observed reflections (R' 0.071). Structure factors are deposited as Supplementary Publication No. SUP 21563 (4 pp.).* Final positional and thermal parameters for non-hydrogen and hydrogen atoms are given in Tables 1 and 2, and bond distances and angles in Table 3.

TABLE 1

Final positional (fractional) and thermal * parameters ($\times$ 10^4) for non-hydrogen atoms, with standard deviations in parentheses.

	x	y	z
Br	950(1)	3 868(2)	2 051(2)
C(1)	9 431(8)	3 940(20)	2 020(20)
C(2)	9 000(10)	4 950(10)	2 970(20)
C(3)	7 900(10)	4 980(10)	3 030(20)
C(4)	7 283(9)	4 080(10)	2 040(20)
C(5)	7 740(10)	3 100(10)	1 080(20)
C(6)	8 830(10)	3 020(10)	1 060(20)
C(7)	5 542(9)	4 570(10)	930(20)
C(8)	4 332(8)	4 660(10)	760(10)
C(9)	3 810(10)	3 280(10)	490(20)
C(10)	6 120(10)	390(20)	2 710(20)
N	6 137(7)	4 060(10)	2 150(10)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	58(1)	241(3)	440(5)	6(1)	28(2)	29(2)
C(1)	29(8)	170(20)	337(34)	22(13)	17(14)	90(25)
C(2)	66(12)	111(18)	386(36)	−2(13)	8(15)	−32(23)
C(3)	85(13)	136(20)	315(36)	10(13)	−16(17)	−23(22)
C(4)	71(10)	159(20)	220(20)	11(13)	34(15)	58(22)
C(5)	73(11)	165(21)	282(33)	−5(13)	23(15)	−5(21)
C(6)	64(11)	187(21)	261(31)	−7(13)	20(14)	−38(20)
C(7)	60(10)	127(16)	259(30)	−8(10)	20(13)	26(19)
C(8)	57(10)	124(16)	215(28)	−2(9)	7(12)	24(18)
C(9)	89(11)	135(18)	316(37)	−24(12)	−1(16)	14(21)
C(10)	80(11)	200(22)	246(31)	−21(14)	45(17)	−6(22)
N	60(7)	158(14)	288(22)	4(9)	24(10)	10(16)

* Anisotropic temperature factors are in the form: exp-$(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

TABLE 2

Positional (fractional $\times$ 10^3) and thermal parameters for the hydrogen atoms, with estimated standard deviations in parentheses

	x	y	z	B/Å^2
H(3)	754(9)	570(10)	380(10)	6.0
H(2)	950(10)	550(10)	420(10)	5.8
H(5)	739(9)	260(10)	30(10)	5.7
H(6)	922(9)	230(10)	20(10)	5.7
H(10)	590(10)	990(20)	160(20)	6.1
H(12)	680(10)	70(10)	280(20)	6.1
H(11)	580(10)	140(10)	270(20)	6.1
H(8)	380(10)	230(10)	170(20)	6.5
H(9)	420(10)	280(10)	950(20)	6.5
H(7)	320(10)	330(10)	970(20)	6.5

DISCUSSION

The structure of the di-imine (III) is shown in Figure 1.[7] Although solution studies have indicated that various di-imines of the cyclobutanedione system exist in both the *cis*- and ***trans***-configurations,[8] compound (III) in the crystalline state is ***trans***, as established by the presence of an inversion centre.

The cyclobutane ring of the di-imine (III) is planar, as required by the crystal symmetry. A least-squares plane calculation for the benzene ring yields individual deviations of 0.08, − 0.02, 0.02, −0.01, −0.004, and 0.005 Å for C(1)—(6). This ring makes an angle of *ca.* 68° with the four-membered ring. Any changes of the transannular distance in (I), (II), or (III) should therefore be a result of the influence of the respective functional groups, since both (I) and (II) have also been shown to be planar.[1,2] However, bond distances and bond angles are not significantly different

TABLE 3

Distances (Å) and angles (°)

(*a*) Distances			
Br–C(1)	1.92(1)	C(1)–C(6)	1.37(2)
C(1)–C(2)	1.39(2)	C(5)–C(6)	1.38(2)
C(2)–C(3)	1.40(2)	C(7)–C(7′)	2.08(2)
C(3)–C(4)	1.38(2)	C(6)–H(6)	1.1(1)
C(4)–C(5)	1.38(2)	C(9)–H(7)	0.9(1)
N–C(4)	1.46(1)	C(9)–H(8)	1.3(1)
C(7)–N	1.26(2)	C(9)–H(9)	1.0(1)
C(8)–C(7)	1.53(2)	C(10)–H(10)	1.0(1)
C(8)–C(9)	1.55(1)	C(10)–H(11)	1.1(1)
C(8)–C(10)	1.52(2)	C(10)–H(12)	0.9(1)
C(2)–H(2)	1.2(1)		
C(3)–H(3)	1.0(1)		
C(5)–H(5)	0.9(1)		
(*b*) Angles			
Br–C(1)–C(2)	117(1)	C(7)–N–C(4)	119(1)
Br–C(1)–C(6)	119(1)	C(8)–C(7)–N	129(1)
C(2)–C(1)–C(6)	123(1)	C(8)–C(7)–C(8′)	93.9(9)
C(1)–C(2)–C(3)	118(1)	H(7)–C(9)–C(8)	113(9)
C(2)–C(3)–C(4)	119(1)	H(8)–C(9)–C(8)	126(6)
C(3)–C(4)–C(5)	121(1)	H(9)–C(9)–C(8)	107(6)
C(4)–C(5)–C(6)	120(1)	H(10)–C(10)–C(8)	108(7)
C(5)–C(6)–C(1)	118(1)	H(11)–C(10)–C(8)	107(8)
N–C(4)–C(3)	120(1)	H(12)–C(10)–C(8)	121(9)
N–C(4)–C(5)	118(1)	C(7)–C(8)–C(9)	111.8(9)
C(7)–C(8)–C(7′)	86.1(9)	H(3)–C(3)–C(4)	120(6)
C(7)–C(8)–C(10)	113.3(9)	H(5)–C(5)–C(4)	124(7)
C(9)–C(8)–C(10)	111(1)	H(5)–C(5)–C(6)	114(7)
H(2)–C(2)–C(1)	122(6)	H(6)–C(6)–C(1)	120(6)
H(2)–C(2)–C(3)	115(6)	H(6)–C(6)–C(5)	122(6)
H(3)–C(3)–C(2)	120(6)		

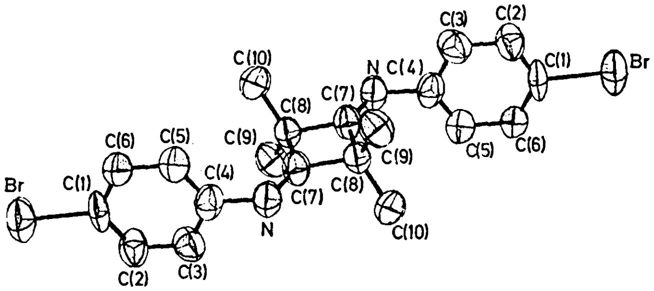

FIGURE 1 Molecular structure of (III)

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[7] C. K. Johnson, 'ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations,' Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

[8] J. J. Worman and E. A. Schmidt, *J. Org. Chem.*, 1970, **35**, 2463.

from those observed for cyclobutanedione[1] and cyclobutanedithione.[2] Table 4 summarizes the ring bond parameters for structures (I)—(III).

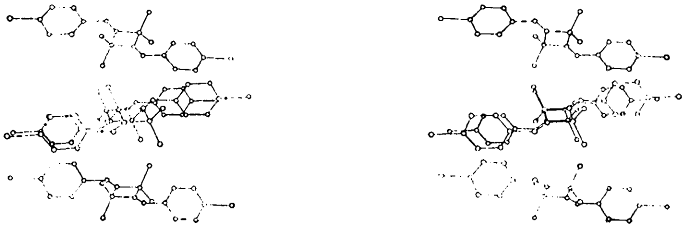

FIGURE 2 Stereogram of (III)

It is important to recognize that the carbon–nitrogen normal single-bond distance is 1.472 Å[9] compared to that observed in our system of 1.46(1) Å [N—C(4)]. This means that the nitrogen $2p$ electrons are not in resonance with the benzene ring and a comparison of transannular distance in (I)—(III) is valid.

TABLE 4

Bond parameters of cyclobutane compounds (distances Å, angles °)

	(I)	(II)	(III)
M–C(7)	1.20	1.599(7)	1.26(2)
C(7)–C(8)	1.54	1.520(6)	1.53(2)
C(7)–C(8′)	1.51	1.520(6)	1.53(2)
C(8)–C(9)	1.53	1.523(6)	1.55(1)
C(8)–C(10)	1.53	1.523(6)	1.52(2)
C(7)–C(7′)	2.078	2.071(7)	2.08(2)
C(7)–C(8)–C(7′)	85	86.5(5)	86.1(9)
C(8)–C(7)–C(8′)	95	93.5(6)	93.8(9)

The C(7) and C(7′) distance in (III) is also the same (2.08 Å) as in (I) and (II). The functional group does not alter the transannular distance of the cyclobutane ring. Thus the differences in u.v.–visible spectroscopic observation for these systems[10] are not a result of the distance across the ring.

The molecular packing in di-imine (III) is illustrated in Figure 2. The closest intermolecular contact is 1.96 Å between H(2) and its inversion-related equivalent.

Since the cyclobutane rings in compounds (I)—(III) are identical, differences in the u.v.–visible spectroscopic properties of these systems must result from the differences in the non-bonding orbital energies of the respective non-carbon atoms. This has been partially established by photoelectron spectroscopy[11,12] and we tend to agree with these results rather than with the long-held concept that there is $p\pi$-type overlap across the ring.

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[5/381 *Received, February 24th,* 1975]

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[9] ' International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, 1962.

[10] K. E. Ballard and C. H. Park, *Spectrochim. Acta.*, 1970, **26A**, 43.

[11] D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbrower, and V. Hornung, *Angew. Chem. Internat. Edn.*, 1971, **10**, 401.

[12] R. A. W. Johnstone, personal communication.