cytosine monohydrate should be of marginal significance, in agreement with our findings.

This work was supported by Grant Nos. NS-02763 and GM-01728 of the U.S. Public Health Service, National Institutes of Health. The IBM 1130 and 7090 computer programs used were those written or modified by Dr R. Shiono and J. Rutherford.

References

BARKER, D. L. & MARSH, R. E. (1964). *Acta Cryst.* **17**, 1581–1587.

CRAVEN, B. M., CUSATIS, C., GARTLAND, G. L. & VIZZINI, E. A. (1973). *J. Mol. Struct.* In the press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JEFFREY, G. A. & KINOSHITA, Y. (1963). *Acta Cryst.* **16**, 20–38.

PIMENTEL, G. C. & MCCLELLAN, A. L. (1959). *The Hydrogen Bond.* San Francisco: Freeman.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VOET, D. & RICH, A. (1970). *Prog. Nucleic Acid Res. Mol. Biol.* **10**, 183–264.

Acta Cryst. (1973). B**29**, 1238

The Crystal Structure of Naphtho[*b*]cyclobutene*

BY JAMES L. CRAWFORD† AND RICHARD E. MARSH

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, *U.S.A.*

(*Received* 28 *December* 1972; *accepted* 5 *February* 1973)

Crystals of naphtho[*b*]cyclobutene, $C_{12}H_{10}$, are monoclinic, space group $P2_1/c$, with $a=5{\cdot}796$ (2), $b=18{\cdot}015$ (8), $c=8{\cdot}291$ (3) Å, $\beta=106{\cdot}50$ (3)°. A structure determination, based on 1228 reflections measured on a diffractometer, led to an R index of 0·035 and estimated deviations of about 0·0015 Å in the coordinates of the C atoms and 0·015 Å in the coordinates of the H atoms. The fusion of the cyclobutene ring results in small distortions in the naphthalene grouping, presumably due to bond-angle constraints at C(2) and C(3).

Introduction

This work is part of a program of studies on the geometries of strained fused-ring compounds.

Experimental

Crystals of naphtho[*b*]cyclobutene, which was first synthesized by Cava & Shirley (1960), were supplied by Dr Ashley Cooper of the Jet Propulsion Laboratory, Pasadena. They were colorless prisms, somewhat elongated along **a**. They sublime slowly at room temperature. The crystal used in this work had dimensions 0·36 × 0·30 × 0·30 mm (along **a**, **b** and **c**) and was sealed in a 0·3 mm diameter thin-walled glass capillary to prevent sublimation. Preliminary rotation and Weissenberg photographs showed monoclinic symmetry with systematic absences ($h0l$, l odd; $0k0$, k odd) characteristic of space group $P2_1/c$. The crystal was then mounted on a General Electric quarter-circle diffractometer, automated by Datex and highly modified by Dr Sten Samson. Cell dimensions were obtained from a least-squares fit to 2θ values for 15 reflections; they are given in Table 1. We did not measure the crystal density.

Table 1. *Crystal data*

Naphtho[*b*]cyclobutene	$C_{12}H_{10}$
Monoclinic	F.W. 154·2
Space group, $P2_1/c$	m.p. 86 °C*
$a=$ 5·796 (2) Å	$Z=4$
$b=18{\cdot}015$ (8)	$F(000)=328$
$c=$ 8·291 (3)	$D_x=1{\cdot}23$ g cm^{-3}
$\beta=106{\cdot}50$ (3)°	$\mu=4$ cm^{-1}
$V=830{\cdot}1$ (9) Å^3	λ(Cu $K\alpha$) = 1·5418 Å

* Cava & Shirley (1960).

Intensities were measured using Cu $K\alpha$ radiation and θ–2θ scans at a speed of 2° (in 2θ) per min; backgrounds were counted for 30 sec at the extrema. The $11\bar{2}$ reflection was monitored every 20 reflections; its intensity decreased from 864,000 to 820,000 counts – about 5% – during the one-week period of data collection. All reflections in one quadrant of reciprocal space out to $2\theta=130°$ were surveyed; they numbered 1236, of which 49 had net intensities less than zero. Six reflections ($\bar{5}74$; $\bar{1},17,1$; $\bar{1},17,2$; $\bar{1}85$; $\bar{1}95$; and $\bar{1},10,5$) were not recorded because of failures

---

* Contribution No. 4599 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109.

† Present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

of the apparatus, while three reflections (100; $\bar{1}22$; and $\bar{1}32$) had intensities that exceeded the capacity of the instrument (10^6 counts). The intensity of the $\bar{1}22$ reflection was eventually corrected for the overflow; the 100 and $\bar{1}32$ reflections were not corrected satisfactorily.

Observational variances $\sigma^2(I)$ were based on counting statistics plus an additional term $(0{\cdot}02S)^2$, where S is the scan count. Intensities and their standard deviations were corrected for Lorentz and polarization effects and for crystal decay as indicated by the check reflection, but not for absorption ($\mu r_{\max} \sim 0{\cdot}16$).

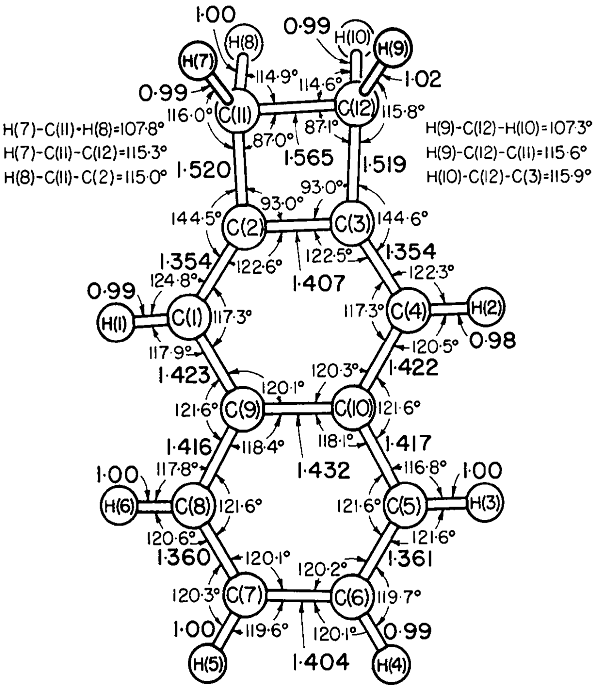


Fig. 1. Bond distances and angles. Standard deviations are about 0·002 Å in the C–C distances, 0·015 Å in the C–H distances, 0·1° in the C–C–C angles, 0·6° in the C–C–H angles and 0·9° in the H–C–H angles.

Structure determination and refinement

Positions of the ten carbon atoms of the naphthalene moiety were derived from sharpened and unsharpened Patterson maps, and the two remaining carbon atoms were recovered from an electron density map. Least-squares refinement of the coordinates and isotropic temperature parameters of these 12 atoms led to an R index of 0·158. Positions of the six hydrogen atoms of the naphthalene group were confirmed from a three-dimensional difference map; tentative positions for the four remaining hydrogen atoms were assigned assuming tetrahedral bonding orbitals about C(11) and C(12).

Final least-squares refinement included, in a single matrix, 150 parameters: coordinates and anisotropic temperature parameters for the 12 carbon atoms, coordinates and isotropic temperature parameters for the 10 hydrogen atoms, a scale factor, and an isotropic extinction parameter (Larson, 1967; equation 3). The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, with weights w equal to $1/\sigma^2(F_{\rm obs}^2)$. Two reflections, 100 and $\bar{1}32$, were assigned zero weight; the remaining 1228 reflections, including those with negative net intensities, were included in the refinement. All calculations were carried out on an IBM 360-75 computer using the CRYM system. Atomic form factors for carbon were from *International Tables for X-ray Crystallography* (1962) and for hydrogen from Stewart, Davidson & Simpson (1965).

Table 2. *Coordinates and temperature parameters for naphtho*[*b*]*cyclobutene*

Anisotropic temperature factors for the carbon atoms are of the form exp $(-b_{11}h^2 \ldots - b_{23}kl)$; isotropic temperature factors for the hydrogen atoms are of the form exp $(-B \sin^2\theta/\lambda^2)$. Standard deviations are in parentheses.

	$x \times 10^4$	$y \times 10^5$	$z \times 10^4$	$b_{11} \times 10^4$	$b_{22} \times 10^5$	$b_{33} \times 10^4$	$b_{12} \times 10^4$	$b_{13} \times 10^4$	$b_{23} \times 10^4$
C(1)	−2099 (2)	5874 (7)	1033 (2)	273 (4)	371 (5)	156 (2)	12 (2)	91 (5)	−21 (2)
C(2)	−1177 (2)	−40 (7)	2011 (1)	309 (4)	334 (4)	142 (2)	− 5 (2)	134 (5)	−25 (2)
C(3)	1240 (2)	− 365 (7)	2993 (1)	319 (4)	346 (5)	138 (2)	13 (2)	105 (5)	−18 (2)
C(4)	2819 (2)	5209 (7)	3025 (2)	280 (5)	411 (5)	155 (2)	6 (3)	75 (5)	−25 (2)
C(5)	3459 (3)	17644 (8)	1947 (2)	367 (6)	378 (6)	211 (3)	−26 (3)	189 (7)	−43 (2)
C(6)	2635 (3)	23643 (8)	953 (2)	506 (7)	347 (6)	269 (3)	−44 (3)	342 (8)	−38 (2)
C(7)	224 (3)	23968 (9)	−25 (2)	534 (7)	340 (5)	244 (3)	28 (3)	300 (8)	2 (2)
C(8)	−1304 (3)	18297 (7)	24 (2)	383 (6)	363 (5)	198 (3)	36 (3)	176 (7)	−4 (2)
C(9)	− 518 (2)	11903 (7)	1021 (1)	318 (5)	320 (4)	150 (2)	16 (2)	151 (5)	−25 (2)
C(10)	1942 (2)	11561 (7)	2018 (2)	314 (5)	334 (5)	155 (2)	− 2 (2)	158 (5)	−33 (2)
C(11)	−1751 (3)	−7655 (8)	2586 (2)	392 (5)	359 (6)	179 (3)	−20 (3)	157 (6)	−18 (2)
C(12)	931 (3)	−7987 (8)	3686 (2)	419 (6)	369 (5)	166 (3)	18 (3)	123 (6)	0 (2)

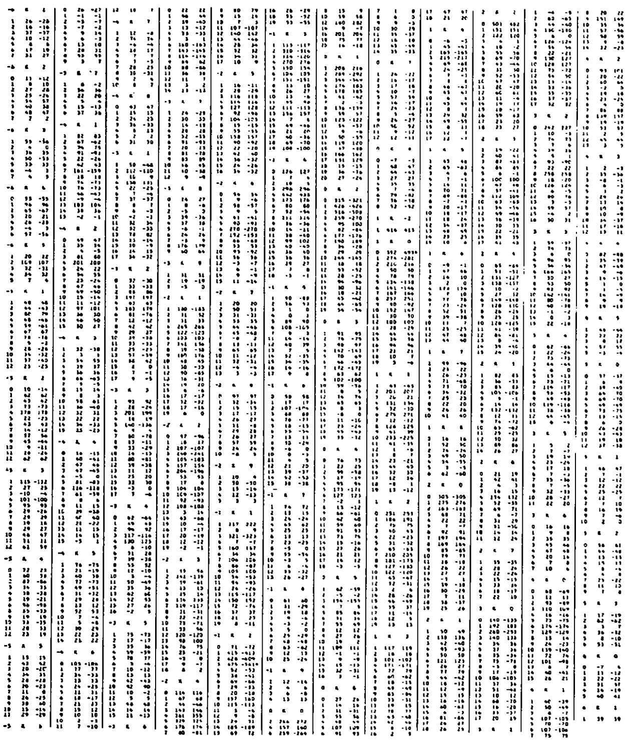
	$x \times 10^3$	$y \times 10^4$	$z \times 10^3$	$B \times 10$		$x \times 10^3$	$y \times 10^4$	$z \times 10^3$	$B \times 10$
H(1)	−379 (2)	630 (6)	32 (2)	50 (3)	H(6)	−303 (2)	1852 (6)	− 66 (2)	54 (3)
H(2)	450 (2)	497 (7)	371 (2)	58 (3)	H(7)	−222 (2)	−1148 (7)	170 (2)	51 (3)
H(3)	516 (2)	1731 (6)	266 (2)	58 (3)	H(8)	−296 (3)	− 767 (7)	323 (2)	56 (3)
H(4)	374 (3)	2778 (8)	93 (2)	66 (4)	H(9)	194 (2)	−1211 (8)	340 (2)	61 (3)
H(5)	− 36 (3)	2839 (8)	− 76 (2)	68 (4)	H(10)	115 (2)	− 823 (7)	491 (2)	54 (3)

$g = 87\ (3) \times 10^{-6}$ (Larson, 1967).

In the last refinement cycle, no coordinate shifted by as much as 0·5σ. The final R index $(=\sum||F_o|-|F_c||/\sum|F_o|)$ for 1179 reflections having net intensities greater than zero is 0·035, and the standard error of fit for all 1228 reflections of non-zero weight is 1·63. Final coordinates are listed in Table 2. Observed and calculated structure factors are listed in Table 3.

Table 3. *Observed and calculated structure factors*

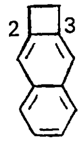
Within each group are given the values of k, $10F_o$, and $10F_c$. A negative sign preceding F_o indicates a negative value for the net intensity; an asterisk following F_c indicates a weight of zero in the final calculations.



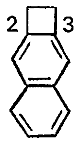
Discussion

Bond distances and angles are shown in Fig. 1. Estimated standard deviations are about 0·002 Å in the C–C distances, 0·015 Å in the C–H distances, 0·1° in the C–C–C angles, 0·6° in the C–C–H angles, and 0·9° in the H–C–H angles. Internal agreement among pairs of equivalent values is, if anything, slightly better than these e.s.d.'s would predict.

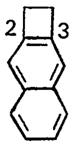
Distances and angles within the naphthalene ring system are in fair agreement with values reported from a neutron diffraction study of perdeuteronaphthalene by Pawley & Yeats (1969) and in X-ray diffraction studies of naphthalene as reported by Cruickshank & Sparks (1962); differences in the C–C bond lengths range up to about 0·02 Å, or about three times the e.s.d.'s in those studies. In the present compound, the fusion of the four-membered ring has produced small but significant distortions within the naphthalene moiety. Differences in bond angles are most prominent; they can be blamed on attempts to relieve the bond-angle strain at C(2) and C(3). The C(1)–C(2) and C(3)–C(4) bonds are about 0·007 Å shorter than the corresponding bonds in the other six-membered ring, and the C(2)–C(3), C(1)–C(9) and C(4)–C(10) bonds are nearly the same amount longer; these differences also seem to be a result of the bond-angle constraints at C(2) and C(3), which would tend to decrease the importance of valence-bond structure (III) relative to (I) and (II).



(I)



(II)



(III)

Deviations from the mean plane of the carbon atoms are given in Table 4. These deviations, though small, are significant; they correspond to folds of about 1°

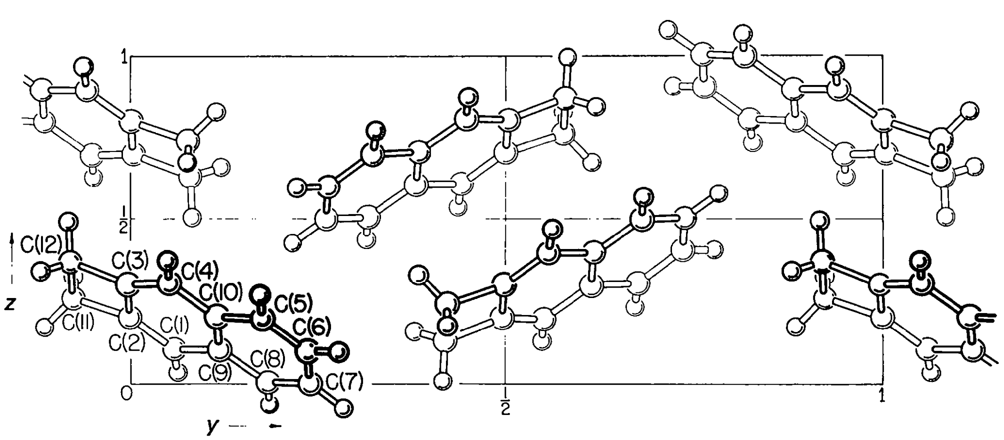


Fig. 2. A drawing of the structure as viewed down the *a* axis.

along the C(9)–C(10) and C(5)···C(8) lines, both in the same sense, and to a very slight buckling of the cyclobutene ring.

Table 4. *Deviations from the least-squares plane*

The normal to the mean plane of the carbon atoms, all weighted equally, has direction cosines of −0·4860, 0·4272, and 0·8691 relative to **a**, **b**, and **c**; the origin-to-plane distance is 1·781 Å.

C(1)	0·006 Å	H(1)	0·01 Å
C(2)	−0·004	H(2)	0·01
C(3)	−0·002	H(3)	0·01
C(4)	0·005	H(4)	−0·03
C(5)	0·005	H(5)	−0·05
C(6)	−0·018	H(6)	0·03
C(7)	−0·018	H(7)	−0·81
C(8)	0·011	H(8)	0·79
C(9)	0·016	H(9)	−0·81
C(10)	0·015	H(10)	0·80
C(11)	−0·014		
C(12)	−0·002		

A packing drawing of the molecule is shown in Fig. 2. The shortest intermolecular distances include H···H, 2·52 Å, and C···H, 2·95 Å; there are no C···C distances below 3·5 Å. Despite this rather loose packing, the temperature factors are relatively small and isotropic. While a rigid-body treatment is not entirely satisfactory, the largest thermal motions are consistent with an in-plane libration of r.m.s. amplitude about 2°, with the axis of libration passing near the center of mass of the molecule. The effects of this motion on the bond distances would be no larger than 0·002 Å or so.

References

Cava, M. P. & Shirley, R. L. (1960). *J. Amer. Chem. Soc.* **82**, 654–656.

Cruickshank, D. W. J. & Sparks, R. A. (1960). *Proc. Roy. Soc.* A**258**, 270–285.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.

Pawley, G. S. & Yeats, E. A. (1969). *Acta Cryst.* B**25**, 2009–2013.

Stewart, R. F., Davidson, G. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1973). B**29**, 1241

The Crystal and Molecular Structure of *S*,*S*-Dimethyl-*N*-trichloroacetyl Sulphilimine, $C_4H_6ONSCl_3$

By A. Kálmán and K. Sasvári

Central Research Institute for Chemistry, Hungarian Academy of Sciences, 1525-*Budapest, PF.* 17, *Hungary*

and Á. Kucsman

Institute of Organic Chemistry, L. Eötvös University, Budapest, Hungary

(*Received* 7 *February* 1973; *accepted* 8 *February* 1973)

S,*S*-Dimethyl-*N*-trichloroacetyl sulphilimine (DMTAS) crystallizes in the orthorhombic space group $P2_12_12_1$, with $a=8{\cdot}934$ (5), $b=9{\cdot}317$ (5), $c=10{\cdot}952$ (6) Å, $Z=4$. The structure was solved by direct methods and refined by least-squares calculations to an *R* value of 0·060 with 939 diffractometric intensities. All hydrogen atoms were located in a difference Fourier synthesis. The S(IV)–N(sp^2) bond length (1·667 Å) is similar to that of 1·673 Å observed in *S*,*S*-diethyl-*N*-dichloroacetyl sulphilimine, but considerably longer than those found in several *N*-sulphonyl sulphilimines. It can, however, be regarded as a partial π bond involved in the mesomerism of the SNCO group. The electronic structure and conformation of the molecule are discussed.

Introduction

An X-ray study of *S*,*S*-dimethyl-*N*-trichloroacetyl sulphilimine (DMTAS; $Me_2S{:}N.CO.CCl_3$) has been carried out in order to gain support for the conclusions drawn from the structure determination (Kálmán, Sasvári & Kucsman, 1971) of *S*,*S*-diethyl-*N*-dichloroacetyl sulphilimine (DEDAS; $Et_2S{:}N.CO.CHCl_2$), namely (i) there is an $>S{=}N{-}C{=}O \leftrightarrow >\overset{+}{S}{-}N{=}C{-}\overset{-}{O}$ resonance in the fairly planar S, N, C(2), O, C(1) moiety; (ii) the S(IV)–N(sp^2) bond of intermediate bond order is significantly (Cruickshank & Robertson, 1953) longer and therefore weaker than in *N*-sulphonyl sulphilimines (Kálmán, 1967; Kucsman, Kálmán & Kapovits, 1967; Kálmán, Duffin & Kucsman, 1971; Cameron, Hair & Morris, 1971; Kálmán & Sasvári, 1972) [1·673 *vs.* 1·620–1·636 Å,]; (iii) sulphur and oxygen atoms are in a *cis* arrangement.

Experimental

DMTAS was prepared and kindly provided by Dr I. Kapovits. Infrared and melting point data showed that