CRYSTAL AND SOLUTION STRUCTURE OF (*E*)-1,2-BIS(ETHYLSULPHONYL)CYCLOBUTANE-1,2-DICARBONITRILE

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The unusual product of the reaction of 2-chloroacrylonitrile with ethane thiol and following hydrogen peroxide oxidation was found to be (*E*)-1,2-bis(ethylsulphonyl)cyclobutane-1,2-dicarbonitrile by means of X-ray crystallography. ^{1}H and ^{13}C NMR study of this compound has proven the same conformation of the molecule in solution.

The reaction of 2-chloroacrylonitrile with ethane thiol catalyzed by sodium tert--butanolate in benzene, originally[1] intended to afford 3-ethylthio-2-chloropropionitrile gave, instead, a cyclobutane derivative formed presumably by a cyclodimerization reaction[2,3] of an unsaturated intermediate. The aim of this work is to determine the structure of the corresponding, well crystallizing sulphone obtained by oxidation of the original prouct by hydrogen peroxide in acetic acid.

RESULTS AND DISCUSSION

For an R_2,R'_2-tetrasubstituted cyclobutane derivative with substituents in two geminal positions (1,1,2,2- and/or 1,1,3,3-tetrasubstituted) there are six theoretically possible isomers *I* — *VI* shown in Fig. 1. Structures *I* — *IV* represent the *meso*-forms while the two last structures *V* and *VI* are achiral.

First information on the structure of reaction product was derived from ^{13}C and ^{1}H NMR spectra in hexadeuterodimethylsulphoxide. Proton decoupled "attached proton test" ^{13}C NMR spectrum[4] gave five signals — three of them belonging to the substituents $(CH_3-CH_2-SO_2$ and $CN)$ and only two signals for the ring carbon atoms $(-\overset{|}{\underset{|}{C}}-, -CH_2-)$ — for the data see Table I. This is in general accordance with the structure and symmetry features of isomers *I* — *IV*. Structures *V*

and *VI* with two identical substituents on the same carbon atom would give 7 and 6 signals resp. (four and/or three different signals for ring carbon atoms) and these isomers could be, therefore, excluded. Proton NMR spectrum (data in Table I) proved the presence of ethylsulphonyl protons and showed one sharp singlet at δ 3·00 for all four cyclobutane protons. From the inspection of the structures $I-IV$ it follows that cyclobutane protons in $I-III$ would give AA'BB' spectra and only for isomer *IV* we can expect the A_4 spin system with a singlet in the ^1H NMR spectrum. Hence, the structure *IV* was suggested for reaction product on the basis of the ^1H and ^{13}C NMR data.

A different picture was, however, obtained by X-ray crystallography. The crystal structure consists of discrete molecules (Fig. 2) arranged at van der Waals or longer distances (Fig. 3). The molecular packing is very loose with only four C···C contacts shorter than 4 Å and no contact involving the O and/or N atoms below 3·2 Å (hydrogen atoms not assumed). The imposed crystallographic C_2 axis passing through the middle of the C(1)—C(1') and C(2)—C(2') bonds requires the molecule to adopt the (E)-1,1',2,2'-tetrasubstituted configuration, corresponding to the opposite chirality at C(1) and C(1') (i.e., the *meso*-form *I*).

It is well known that cyclobutane and its substituted derivatives prefer a puckered conformation of the ring. The arrangement characterized by the dihedral angle of
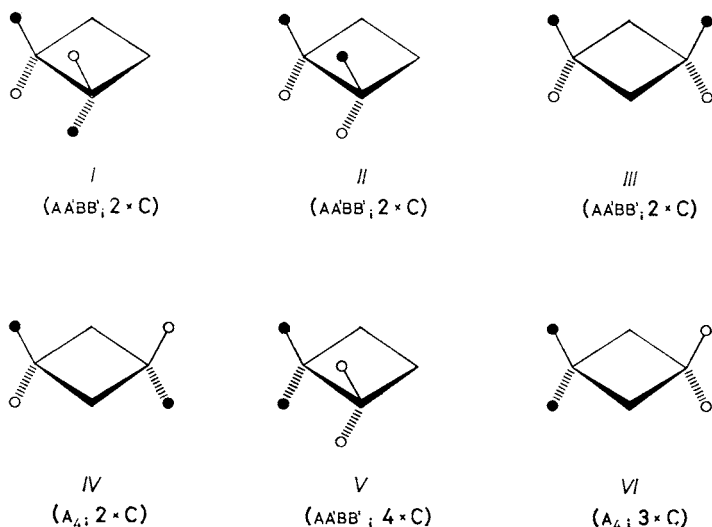

FIG. 1

Theoretically possible isomers of 1,1,2,2- and 1,1,3,3-R_2,R_2'-tetrasubstituted cyclobutanes (O = CN, ● = SO$_2$Et). The corresponding type of the spin system of ring protons and the number of the expected signals of ring carbon atoms are given in parentheses

TABLE I

Carbon-13 and proton NMR parameters (δ, ppm; J, Hz) of compound *I*

Solvent	^{13}C Chemical shifts				
	CH$_2$	>C<	SO$_2$CH$_2$	CH$_3$	C≡N
CD$_3$SOCD$_3$	27·14	58·21	45·03	5·89	112·93
CD$_3$COCD$_3$	28·01	59·61	45·91	5·98	113·50

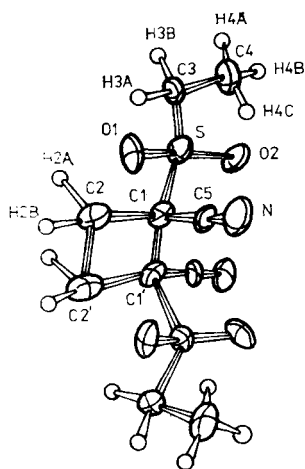|	^{1}H NMR parameters		
	CH$_2$	SO$_2$CH$_2$	CH$_3$
CD$_3$SOCD$_3$	3·00 s	3·79 dq 3·62 dq $^2J = -14·0$ $^3J = 7·45$	1·42 t $^3J = 7·45$
CD$_3$COCD$_3$	3·264 (A, A'); 3·242 (B, B') $J(A, B) = J(A', B') = -13·27$ $J(A, B') = J(B, A') = 10·09$ $J(A, A') = 8·35$ $J(B, B') = 3·24$	3·90 dq 3·80 dq $^2J = -13·85$ $^3J = 7·45$	1·70 t $^3J = 7·45$

FIG. 2

Perspective view of the molecule with atom
numbering (only the independent half and
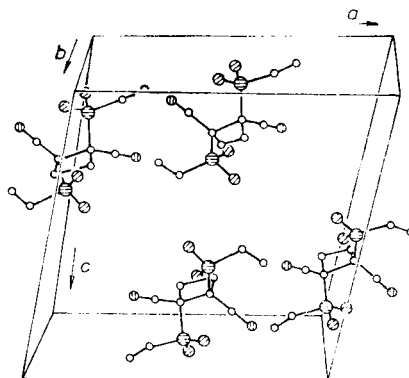the directly joined atoms are numbered)

FIG. 3

Unit cell content

ca. 18° to 31°, typical for a number of derivatives in the gaseous as well as in the solid state[5,6], has a barrier to inversion of some $5-7$ kJ mol^{-1}; hence, the uncommon planar arrangement should be regarded as a transition state, usually stabilized by imposed crystallographic symmetry, i.e. by packing forces. The present structure conforms to the picture of the puckered ring. It differs, however, in that the dihedral angle of the C(1), C(1'), C(2) and C(1), C(2), C(2') planes is only 12·8(6)°. Neither packing effects (vide supra) nor the electronegativity of the substituents[7] are likely to be responsible for this. Close inspection of other geometrical parameters suggests, however, that the probable reason for flattening of the ring is the bulkiness of the ethylsulphonyl substituents. Comparison of the bond lengths with average values compiled for a number of related structures[8] support this explanation. In the title structure, there are only two bond lengths which exceed these averages by more than 1 esd of the mean, both involving the C(1) atom: C(1)—C(1') 1·592(4) Å (the average is 1·554(21) Å) and C(1)—S 1·839(2) Å (av. 1·782(18) Å). Similar effects on the bond lengths and on the dihedral angle are operative for a related cyclobutane derivative[9] which can also be regarded as overcrowded.

All other bond distances, valence and torsion angles adopt usual values with the exception of the conformation of the SO$_2$ group which is twisted away from the nitrile group bonded to the adjacent carbon atom, resulting in the N···O contacts of 3·346(2) and 3·517(2) Å. Undoubtedly, this arrangement minimizes mutual repulsions of the electronegative substituents.

The final atomic coordinates are listed in Table II, the bond lengths and angles in Table III.*

To explain the inconsistence between X-ray derived structure *I* and ^{1}H NMR spectrum discussed above and suggesting structure *IV* we have repeated the NMR experiment using hexadeuteroacetone (instead of hexadeuterodimethylsulphoxide) as solvent. ^{13}C NMR spectrum showed the same number of signals with slightly changed chemical shift values (Table I). Fortunately, ^{1}H NMR spectrum gave a different spectral pattern of cyclobutane protons as a multiplet of an AA'BB' spin systems in accordance with expectation for the X-ray structure. It means that the previous ^{1}H NMR spectrum in CD$_3$SOCD$_3$ showed virtually higher symmetry due to accidentally identical shielding effects (chemical shifts) on all cyclobutane protons in this solvent.

Simulation-iteration analysis of the AA'BB' part of ^{1}H NMR spectrum in acetone afforded a complete set of accessible proton NMR parameters (Table I). Similar coupling constant set was described for (*E*)-1,2-bis(chloro)-1,2-dicarbonitrile in ref.[10]. Vicinal coupling constants of *I* (Table I) were then used for the estimation of partial geometry (ring puckering) in solution. Appropriately adjusted Karplus-

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* Tables of structure factors, anisotropic temperature parameters, hydrogen atom coordinates and further experimental details are available from the authors upon request.

-like equation for cyclobutane systems is difficult to find in the literature. Therefore, we have prefered the method of Slessor and Tracey[11] which does not require the

TABLE II

Atomic coordinates ($. 10^4$) of non-hydrogen atoms with estimated standard deviations in parentheses. $U_{eq} = 1/3 \sum_i \sum_j a_i a_j a_i^* a_j^* U_{ij}$

Atom	x/a	y/b	z/c	$U_{eq}(. 10^4)$, Å^2
S	5 170·8(4)	1 916(1)	1 149·4(3)	321(3)
O(1)	4 416(1)	3 433(3)	787(1)	455(7)
O(2)	4 965(1)	−443(3)	1 128(1)	419(7)
C(1)	5 479(2)	2 710(4)	2 282(1)	305(8)
C(2)	5 522(2)	5 325(4)	2 396(2)	415(9)
C(3)	6 249(2)	2 484(6,	710(2)	466(10)
C(4)	6 943(3)	481(7)	736(3)	628(14)
C(5)	6 317(2)	1 382(5)	2 682(2)	361(8)
N	7 011(2)	413(4)	2 960(2)	514(9)

TABLE III

Bond lengths (in Å) and angles (in °) with estimated standard deviations in parentheses. Symmetry code: '), $1 - x, y, 1/2 - z$

Bond lengths		Bond angles	
S—O(1)	1·428(2)	O(1)—S—O(2)	118·8(1)
S—O(2)	1·435(2)	O(1)—S—C(1)	105·3(1)
S—C(1)	1·837(2)	O(1)—S—C(3)	109·1(1)
S—C(3)	1·783(3)	O(2)—S—C(1)	106·8(1)
C(1)—C(2)	1·570(4)	O(2)—S—C(3)	110·7(1)
C(1)—C(5)	1·459(4)	C(1)—S—C(3)	105·1(1)
C(1)—C(1')	1·595(5)	S—C(1)—C(2)	111·5(2)
C(2)—C(2')	1·536(4)	S—C(1)—C(5)	108·8(2)
C(3)—C(4)	1·529(5)	S—C(1)—C(1')	110·5(3)
C(5)—N	1·145(4)	C(2)—C(1)—C(5)	118·5(2)
		C(2)—C(1)—C(1')	88·2(2)
		C(5)—C(1)—C(1')	118·1(3)
		C(1)—C(2)—C(2')	90·3(2)
		S—C(3)—C(4)	113·9(2)
		C(1)—C(5)—N	175·4(2)

knowledge of accurate values of coefficients in the Karplus equation. Using 0·9 as a well estimated value for the k_1/k_2 ratio (ref.[11]) we could calculate Φ_1 (the dihedral angle H(A)—C—C—H(B') ≡ H(B)—C—C—H(A')) and ω (the projection of bond angle H(A)—C—H(B) ≡ H(A')—C—H(B')) as equal to 12·5° and 135°, respectively. All dihedral angles of protons on the —CH$_2$—CH$_2$— fragment of cyclobutane ring are then defined as shown in Fig. 4. As it follows from Fig. 4, we can expect the value of about 12·5° also for the dihedral angle C—CH$_2$—CH$_2$—C in perfect agreement with the value of 12·8° found from X-ray analysis, so indicating very similar geometry of molecule *I* in crystal and in solution.

EXPERIMENTAL

A polycrystalline material, m.p. 156—157°C, was kindly provided by Dr J. Poláková. For $C_{10}H_{14}N_2O_4S_2$ (290·4) calculated: 41·37% C, 4·86% H, 22·08% S; found: 41·14% C, 4·93% H, 22·19% S.

^{1}H and ^{13}C NMR spectra were measured on a FT-NMR spectrometer Varian XL-200 (at 200 MHz and 50·3 MHz, resp.) in CD$_3$SOCD$_3$ and CD$_3$COCD$_3$ solution. Solvent signals were used for referencing spectra in the following way (CD$_3$SOCD$_3$: δ(H) = 2·50 and δ(C) = 39·7; CD$_3$COCD$_3$: δ(H) = 2·20 and δ(C) = 29·8). Simulation-iteration analysis of the ^{1}H NMR spectrum of cyclobutane protons (AA′BB′ spin system) in CD$_3$COCD$_3$ was performed using LAME program (standard part of Varian software version H1Z).

Single crystals for X-ray diffraction were grown by cooling slowly a hot 3% solution of *I* in ethanol. The density was determined by flotation in tetrachloromethane–hexane. Crystal data: monoclinic, space group $C2/c$, $a = 13·856(3)$, $b = 5·963(1)$, $c = 15·895(3)$ Å, $\beta = 99·70(2)°$, $V = 1\ 291·6(4)$ Å^3, $Z = 4$, $\varrho_m = 1·485(3)$, $\varrho_c = 1·493$ cm^{-3}, $F(000) = 608$. Measurement an 0·18 × 0·23 × 0·25 mm^3 fragment of a large needle-like crystal, Syntex P2$_1$ diffractometer
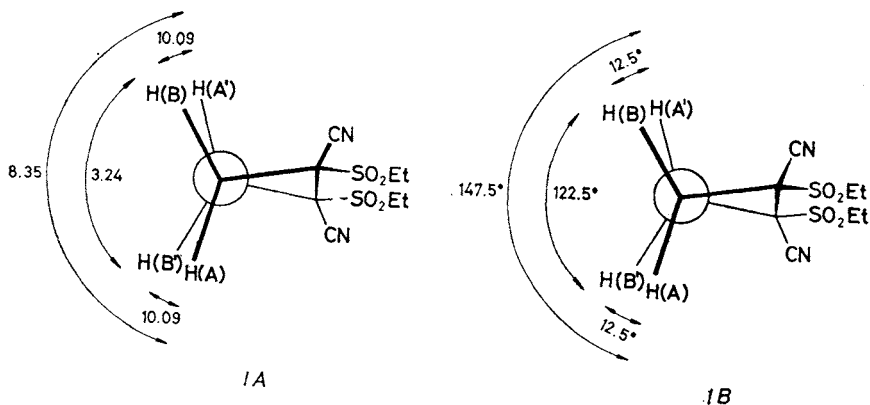

FIG. 4

Experimental values of vicinal interproton coupling constants (*IA*) and calculated dihedral angles of protons (*IB*) for compound *I* in hexadeuteroacetone

$\lambda(CuK_\alpha) = 1.5418$ Å, 295 K, $\mu = 3.76$ mm^{-1}, lattice parameters determined from 16 reflections ($5.5° < \Theta < 14.5°$), $\Theta–2\Theta$ scan mode, $0 \leqq h \leqq 14$, $0 \leqq k \leqq 6$, $-16 \leqq l \leqq 17$, max. value of $\sin \Theta/\lambda = 0.645$ Å^{-1}; 3 standard reflections monitored after every 30 showed no significant fluctuation; from a total of 879 independent reflections, 867 were regarded as "observed" ($I > 1.96 \sigma(I)$); absorption correction applied assuming a spherical shape. Structure solution and refinement: direct methods (SHELXS-86, ref.[12]), full-matrix least-squares refinement (SHELX-76, ref.[13]) including coordinates and anisotropic thermal parameters of non-H atoms; all H atoms were clearly visible in the difference map; their individual isotropic thermal parameters were refined but their coordinates were constrained at theoretical positions since, on attempted refinement, they tend to become ill-defined; the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = (\sigma_F^2 + 0.0009|F_o|^2)^{-1}$; the last cycle had $(\Delta/\sigma)_{max} = 0.11$, -0.20, the difference map was featureless with a maximal residual electron density of 0.37, -0.47 e Å^{-3}, $R = 0.052$, $wR = 0.060$.

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