Determination of the Absolute Configuration of (−)-*N*-Ethyl-*N*-methylaniline Oxide by *X*-Ray Analysis: The Molecular Geometry of an *N*-Oxide Salt

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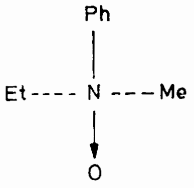
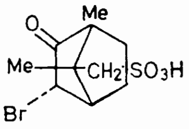
The crystal structure of the (+)-3-bromocamphorsulphonate salt of (−)-*N*-ethyl-*N*-methylaniline oxide has been determined in order to establish the absolute configuration of the *N*-oxide. The crystals of the salt are monoclinic with a = 14·620(4), b = 7·062(5), c = 11·534(5) Å, β = 114° 42′(1′), Z = 2, space group $P2_1$. The structure was refined to a crystallographic R-factor of 0·050 on 1669 non-zero reflections measured on a diffractometer. The absolute configuration of the *N*-oxide was established as *S* by internal comparison to the known absolute configuration of the anion, thus confirming an assignment made previously on the basis of n.m.r. spectral non-equivalence. The important structural parameters in the salt are compared with those in other known structures.

THE method devised by Pirkle[1] has been used to establish the absolute configuration of (−)-*N*-ethyl-*N*-methylaniline oxide (I).[2] No previous assignments of absolute configuration to amine oxides[3,4] have involved dialkylarylamine oxides.† The resolution originally reported[5] for (I) involved reaction of the hydrochloride salt with the silver salt of (+)-3-bromocamphor-9-sulphonic acid (II) and recrystallization of the resulting diastereoisomers from ethyl acetate. As the absolute configuration of (II) is known,[6-8] and as the presence of a bromine atom facilitates crystal structure determination in a non-centrosymmetric space group, an X-ray study of the diastereoisomer of the (−)-*N*-ethyl-*N*-methylaniline oxide and the (+)-3-bromocamphor-9-sulphonic acid was undertaken. The assignment of the configuration of the *N*-oxide relative to that of the camphorsulphonate salt will serve to define the absolute stereochemistry. A preliminary report has appeared.[2]



(I)



(II)

EXPERIMENTAL

Materials.—Commercial samples of *N*-ethyl-*N*-methylaniline and *m*-chloroperbenzoic acid were used without further purification. N.m.r. spectra were obtained on a Varian HA 100 spectrometer.

Synthesis and Resolution of N-*Ethyl*-N-*methylaniline Oxide.*—*N*-Ethyl-*N*-methylaniline was oxidized with *m*-chloroperbenzoic acid in dichloromethane. The *N*-oxide formed was extracted into hydrochloric acid (3M) and isolated and resolved as the 3-bromocamphor-9-sulphonate as described by Meisenheimer.[5] The salt thus obtained was shown to contain, at most, 5% of the minor diastereoisomer ($[\alpha]_D$ 52·1 ± 1°) by liberating the amine oxide and observing its n.m.r. spectrum in a chiral solvent; in this way the peaks corresponding to enantiomeric methyl groups indicated the optical purity to be *ca.* 90%. This partially resolved salt (Found: C, 49·21; H, 6·17; N, 3·28. Calc. for $C_{19}H_{28}BrNO_5S$: C, 49·35; H, 6·11; N, 3·02%) was recrystallized from carbon tetrachloride–acetone in order to obtain colourless needles suitable for X-ray analysis.

Crystal Data.—$C_{19}H_{28}BrNO_5S$, M = 462·4, Monoclinic, a = 14·620(4), b = 7·062(5), c = 11·534(5) Å, β = 114° 42′(1′), U = 1081·9 Å^3, D_m = 1·42 (by flotation), Z = 2, D_c = 1·43, $F(000)$ = 480. Systematic absences: $0k0$ when $k = 2n + 1$ indicate space group $P2_1$ or $P2_1/m$; the single enantiomorphic nature of the molecule establishes $P2_1$ as the correct group. Cu-K_α radiation λ = 1·54178 Å; μ(Cu-K_α) = 39·6 cm^{-1}.

The cell parameters were determined from a least-squares refinement on the settings of the four angles for twelve reflections carefully centred on a Picker FACS 1 diffractometer fitted with a scintillation counter, nickel filter, and pulse-height analyser.

Intensity data were collected from a needle-shaped crystal 0·5 × 0·1 × 0·05 mm. The reflections with $2\theta \leq 130°$ were measured by the θ—2θ scan technique at a scan rate of 1 deg min^{-1}. The basewidth of the scan was 2° with a dispersion correction being applied to account for the $\alpha_1 - \alpha_2$ splitting; backgrounds at each limit of the scan were measured for 10 s. 2022 independent reflections were obtained in the range $2\theta < 130°$ of which 1669 were considered to be significantly above background. Corrections were made for Lorentz and polarization effects, but not for absorption.

The position of the bromine atom was readily obtained from a three-dimensional Patterson map and the positions of the remaining non-hydrogen atoms were determined by the heavy-atom method. Full-matrix least-squares refinement of the positional and isotropic thermal parameters for

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† *Note added in proof:* Since submission of this work, a paper has been published (O. Cervinka and O. Kriz, *Coll. Czech. Chem. Comm.*, 1966, **31**, 1910), in which the configurations of *N*-ethyl-*N*-methylaniline oxide and its phosphorus analogue have been correlated by o.r.d. The configuration thus assigned agrees with that determined herein.

[1] W. H. Pirkle and S. D. Beare, *Tetrahedron Letters*, 1968, 2579; W. H. Pirkle, T. G. Burlingame, and S. D. Beare, *ibid.*, p. 5849; W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, 1967, **89**, 5485; 1968, **90**, 6250; 1969, **91**, 5150.

[2] W. H. Pirkle, R. L. Muntz, and I. C. Paul, *J. Amer. Chem. Soc.*, 1971, **93**, 2817.

[3] S. I. Goldberg and F.-L. Lam, *J. Amer. Chem. Soc.*, 1969, **91**, 5113.

[4] M. Moriwaki, S. Sawada, and Y. Inouye, *Chem. Comm.*, 1970, 419.

[5] J. Meisenheimer, *Chem. Ber.*, 1908, **41**, 3966.

[6] F. H. Allen and D. Rogers, *Chem. Comm.*, 1966, 837; *J. Chem. Soc.* (*B*), 1971, 632.

[7] J. A. Wunderlich, *Acta Cryst.*, 1967, **23**, 846.

[8] S. M. Johnson, I. C. Paul, K. L. Rinehart, jun., and R. Srinivasan, *J. Amer. Chem. Soc.*, 1968, **90**, 136.

these atoms gave an R 0·18; all reflections were given unit weight and the quantity minimized was $\Sigma w|F_\mathrm{o} - F_\mathrm{c}|^2$.

The structure of the salt is shown in Figure 1 which indicates that the establishment of the relative configuration at nitrogen depends on distinguishing which of the two single non-hydrogen atom substituents on nitrogen is carbon (methyl) and which is oxygen. Least-squares refinement of the four substituents on nitrogen when they were included with carbon scattering curves gave B_θ values of 4·5(5), 5·7(6), 5·6(6), and 2·8(4) Å^2. The low isotropic temperature factor for the fourth atom (combined with other evidence discussed in the Results section) indicated it to be the oxygen atom. When this atom was included in the refinement with an oxygen scattering curve, the B_θ value became 5·2(3) Å^2.

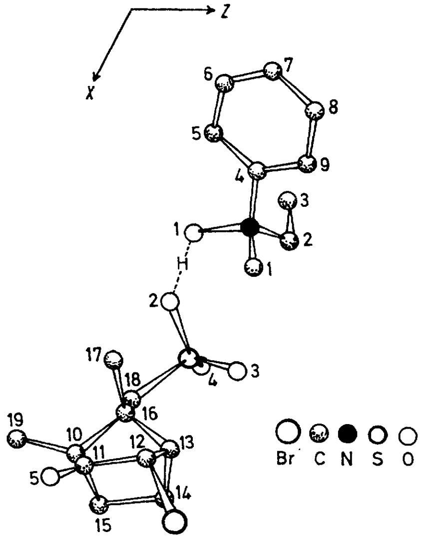

FIGURE 1 View of the molecule looking along b

Least-squares refinement was now continued with the introduction of anisotropic thermal parameters for the atoms. Because of limitations of computer storage the parameters of the camphorsulphonate anion and the N-oxide cation were refined separately. After two cycles of refinement, R was 0·067 and R' was 0·066 $\{R' = [\Sigma w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2/\Sigma w|F_\mathrm{o}|^2]^{1/2}\}$. A difference Fourier map allowed the positions of seventeen of the twenty-eight hydrogen atoms to be established; the positions of the remainder were obtained by applying standard criteria. Further least-squares refinement on the positional and anisotropic thermal parameters of the non-hydrogen atoms and the positional and isotropic thermal parameters of the hydrogen atoms gave R 0·054 and R' 0·048. Upon introduction of anomalous dispersion corrections associated with bromine and sulphur, separate refinement of the two enantiomorphs gave R 0·050 and R' 0·0449 for the S-enantiomorph of the N-oxide and R 0·053 and R' 0·0471 for the R-enantiomorph. The hypothesis that the correct enantiomorph is R can therefore be rejected at the 99·5% significance level.[9] While the absolute configuration of the N-oxide had already been established as S by internal comparison with that of the camphorsulphonate anion,[6] the anomalous dispersion method supports that assignment.

TABLE 1

Final atomic co-ordinates, with standard deviations in parentheses, as fractions of the unit cell edges *

Atom	x	y	z
Br	0·8794(1)	0·2350(4)	0·9248(1)
S	0·5713(1)	0·9231(5)	0·7871(2)
N	0·3274(4)	0·5819(11)	0·7742(5)
O(1)	0·3313(5)	0·6505(11)	0·6618(6)
O(2)	0·4688(3)	0·8867(10)	0·6918(5)
O(3)	0·5957(4)	0·8032(10)	0·8975(5)
O(4)	0·5890(5)	1·1212(10)	0·8196(8)
O(5)	0·8002(4)	0·2982(11)	0·6181(7)
C(1)	0·4045(6)	0·4235(20)	0·8248(10)
C(2)	0·3487(8)	0·7309(21)	0·8711(9)
C(3)	0·2761(17)	0·8975(25)	0·8247(26)
C(4)	0·2227(5)	0·4999(11)	0·7328(7)
C(5)	0·1533(5)	0·5283(15)	0·6084(8)
C(6)	0·0589(7)	0·4449(22)	0·5798(10)
C(7)	0·0346(6)	0·3541(16)	0·6630(9)
C(8)	0·1069(7)	0·3361(17)	0·7871(10)
C(9)	0·2037(6)	0·4070(17)	0·8229(8)
C(10)	0·7545(5)	0·6199(13)	0·6499(7)
C(11)	0·7769(5)	0·4101(16)	0·6789(8)
C(12)	0·7651(6)	0·3736(12)	0·8003(9)
C(13)	0·7449(5)	0·5679(12)	0·8400(7)
C(14)	0·8408(7)	0·6906(15)	0·8774(10)
C(15)	0·8512(6)	0·7168(18)	0·7528(9)
C(16)	0·6769(5)	0·6509(11)	0·7075(7)
C(17)	0·5792(6)	0·5405(16)	0·6326(9)
C(18)	0·6503(7)	0·8618(14)	0·7103(10)
C(19)	0·7281(9)	0·6779(21)	0·5147(11)
H(1a)	0·406(6)	0·338(12)	0·771(8)
H(1b)	0·471(6)	0·499(12)	0·854(7)
H(1c)	0·412(6)	0·369(13)	0·917(9)
H(2a)	0·336(5)	0·690(11)	0·942(7)
H(2b)	0·404(8)	0·801(20)	0·893(11)
H(3a)	0·250(13)	0·935(30)	0·761(15)
H(3b)	0·291(17)	0·961(40)	0·914(20)
H(3c)	0·203(8)	0·857(16)	0·826(11)
H(5)	0·175(7)	0·581(16)	0·540(9)
H(6)	0·034(4)	0·448(11)	0·513(6)
H(7)	−0·039(9)	0·186(26)	0·639(11)
H(8)	0·078(5)	0·274(13)	0·839(7)
H(9)	0·247(6)	0·429(14)	0·907(8)
H(12)	0·724(3)	0·288(6)	0·780(3)
H(13)	0·703(5)	0·557(11)	0·903(6)
H(14a)	0·884(5)	0·623(11)	0·933(7)
H(14b)	0·822(7)	0·834(16)	0·944(9)
H(15a)	0·847(8)	0·859(18)	0·708(10)
H(15b)	0·907(7)	0·674(16)	0·752(9)
H(17a)	0·564(6)	0·592(15)	0·552(9)
H(17b)	0·545(6)	0·490(13)	0·699(8)
H(17c)	0·591(6)	0·422(14)	0·610(8)
H(18a)	0·594(19)	0·967(53)	0·586(25)
H(18b)	0·688(5)	0·901(12)	0·732(7)
H(19a)	0·733(9)	0·815(20)	0·523(12)
H(19b)	0·783(8)	0·640(18)	0·488(10)
H(19c)	0·670(6)	0·602(14)	0·466(8)
H(20)	0·370(5)	0·703(13)	0·684(8)

* The positions and/or thermal parameters of the following hydrogen atoms were somewhat unreasonable after least-squares refinement. The following positions for these atoms were obtained by applying standard criteria:

	x	y	z
H(7)	−0·031	0·302	0·638
H(18a)	0·618	0·903	0·624
H(18b)	0·712	0·929	0·752
H(3b)	0·290	0·986	0·892
H(3c)	0·209	0·854	0·797

Atom H(3a) was reasonably well defined from the difference map and was used along with C(2) to position H(3b) and H(3c).

The largest peak on a final difference map was 0·3 eÅ^{-3} within 0·2 Å of the bromine atom. The positions and/or temperature factors for some of the hydrogen atoms, particularly, H(3a), H(3b), H(3c), H(7), H(18a), and H(18b),

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[9] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

TABLE 2

Anisotropic thermal parameters [a] for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms [b] with estimated standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0·0078(1)	0·0314(3)	0·0282(2)	0·0042(1)	0·0030(1)	0·0037(2)
S	0·0049(1)	0·0247(5)	0·0122(2)	−0·0004(2)	0·0039(1)	−0·0002(3)
N	0·0058(4)	0·0358(20)	0·0083(6)	−0·0052(8)	0·0032(4)	−0·0004(10)
O(1)	0·0079(5)	0·0452(24)	0·0109(7)	−0·0075(9)	0·0038(5)	0·0014(10)
O(2)	0·0048(3)	0·0383(19)	0·0139(6)	−0·0010(7)	0·0034(4)	0·0023(10)
O(3)	0·0066(3)	0·0366(18)	0·0116(6)	0·0016(6)	0·0049(4)	0·0010(9)
O(4)	0·0101(5)	0·0238(16)	0·0309(12)	−0·0019(7)	0·0124(7)	−0·0057(12)
O(5)	0·0074(4)	0·0439(24)	0·0237(10)	−0·0031(8)	0·0070(5)	−0·0178(13)
C(1)	0·0050(5)	0·0458(34)	0·0154(12)	0·0021(12)	0·0041(6)	0·0032(20)
C(2)	0·0103(8)	0·0419(34)	0·0115(10)	−0·0090(17)	0·0058(7)	−0·0049(18)
C(3)	0·0159(16)	0·0334(41)	0·0310(33)	−0·0028(22)	0·0134(20)	−0·0070(33)
C(4)	0·0048(4)	0·0246(19)	0·0113(8)	−0·0016(7)	0·0031(5)	−0·0002(10)
C(5)	0·0045(4)	0·0370(26)	0·0121(9)	−0·0002(9)	0·0020(5)	−0·0009(14)
C(6)	0·0057(6)	0·0559(41)	0·0133(12)	−0·0004(14)	0·0020(7)	0·0009(22)
C(7)	0·0055(5)	0·0466(34)	0·0166(12)	−0·0023(11)	0·0049(7)	−0·0033(16)
C(8)	0·0082(6)	0·0520(40)	0·0174(13)	−0·0058(13)	0·0077(8)	0·0017(18)
C(9)	0·0069(5)	0·0424(31)	0·0118(9)	−0·0048(12)	0·0042(6)	−0·0005(17)
C(10)	0·0056(5)	0·0302(24)	0·0103(8)	−0·0039(8)	0·0043(5)	−0·0059(12)
C(11)	0·0042(4)	0·0363(27)	0·0151(10)	−0·0026(9)	0·0044(6)	−0·0086(16)
C(12)	0·0054(5)	0·0205(18)	0·0172(11)	−0·0014(8)	0·0029(6)	−0·0026(12)
C(13)	0·0053(5)	0·0225(19)	0·0096(7)	−0·0010(8)	0·0026(5)	0·0018(10)
C(14)	0·0053(5)	0·0302(30)	0·0142(11)	−0·0008(9)	0·0005(6)	−0·0028(15)
C(15)	0·0048(4)	0·0354(29)	0·0155(11)	−0·0051(11)	0·0049(6)	−0·0075(16)
C(16)	0·0045(4)	0·0209(17)	0·0093(8)	−0·0019(7)	0·0032(5)	−0·0026(10)
C(17)	0·0052(5)	0·0270(24)	0·0123(10)	−0·0020(9)	0·0030(6)	−0·0011(14)
C(18)	0·0048(5)	0·0246(22)	0·0131(11)	−0·0017(9)	0·0048(6)	−0·0007(12)
C(19)	0·0093(8)	0·0506(48)	0·0145(12)	−0·0050(15)	0·0076(8)	−0·0018(18)

	$B\theta$/Å^2		$B\theta$/Å^2		$B\theta$/Å^2		$B\theta$/Å^2		$B\theta$/Å^2
H(1a)	7(3)	H(3b)	32(8)	H(9)	7(2)	H(15b)	9(3)	H(18b)	3(2)
H(1b)	7(2)	H(3c)	10(11)	H(12)	3(1)	H(17a)	8(3)	H(19a)	9(4)
H(1c)	8(2)	H(5)	10(3)	H(13)	5(2)	H(17b)	6(2)	H(19b)	11(4)
H(2a)	5(2)	H(6)	2(2)	H(14a)	3(2)	H(17c)	7(3)	H(19c)	6(2)
H(2b)	14(4)	H(7)	14(4)	H(14b)	10(3)	H(18a)	54(15)	H(20)	3(2)
H(3a)	19(4)	H(8)	7(2)	H(15a)	10(4)				

[a] The temperature factors are expressed in the form $\exp -[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. [b] The isotropic thermal parameters are expressed as $\exp[-B\theta \sin^2\theta/\lambda^2]$.

resulting from the least-squares refinement are rather unreasonable. However, these co-ordinates were used in both Figure 1 and Table 1. The positional and thermal parameters resulting from the final refinement of the *S*-enantiomorph are listed in Tables 1 and 2; observed and calculated structure factors are listed in Supplementary Publication No. SUP 20275 (3 pp., 1 microfiche).* Atomic scattering factors for neutral carbon, oxygen, nitrogen, bromine, and sulphur were taken from ref. 10 and for hydrogen from ref. 11; the anomalous dispersion terms for bromine and sulphur were taken from ref. 12.

TABLE 3

Bond lengths (Å) with estimated standard deviation in parentheses

N–O(1)	1·409(10)	C(10)–C(11)	1·524(14)
N–C(1)	1·521(14)	C(10)–C(15)	1·573(13)
N–C(2)	1·473(15)	C(10)–C(16)	1·554(11)
N–C(4)	1·515(10)	C(10)–C(19)	1·502(16)
C(2)–C(3)	1·523(26)	C(11)–O(5)	1·197(12)
C(4)–C(5)	1·385(12)	C(11)–C(12)	1·505(14)
C(4)–C(9)	1·354(13)	C(12)–Br	1·952(10)
C(5)–C(6)	1·408(13)	C(12)–C(13)	1·515(12)
C(6)–C(7)	1·322(16)	C(13)–C(14)	1·549(13)
C(7)–C(8)	1·388(15)	C(13)–C(16)	1·550(11)
C(8)–C(9)	1·391(14)	C(14)–C(15)	1·521(15)
S–O(2)	1·465(6)	C(16)–C(17)	1·538(12)
S–O(3)	1·446(7)	C(16)–C(18)	1·542(13)
S–O(4)	1·444(8)		
S–C(18)	1·779(10)		

RESULTS AND DISCUSSION

A drawing of the structure is shown in Figure 1. Bond lengths and angles are listed in Tables 3 and 4.

The assignment of absolute configuration to the amine oxide in this diastereoisomer with the camphorsulphonate anion is based on the determination of the relative configuration at nitrogen. The distinction between carbon and oxygen for the two single-atom substituents is quite unequivocal and is based on several pieces of evidence. Refinement of all four substituents on nitrogen with carbon scattering curves supported the assignment shown in Figure 1 (see Experimental section). Also, the N–O(1) length is 1·409(10) Å [the N–O(H) length[13] in trimethylamine oxide hydrochloride is 1·425(11) Å], compared to 1·515(10), 1·473(15), and 1·521(14) Å for the other three bond lengths involving nitrogen. The difference Fourier map showed three well resolved hydrogen atoms around C(1) and a single hydrogen atom bonded to O(1); the positional and

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[10] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[11] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[12] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 213—216.

[13] A. Caron and J. Donohue, *Acta Cryst.*, 1962, **15**, 1052.

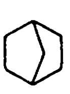
thermal parameters for these four hydrogen atoms after refinement seemed quite reasonable. Finally, the hydrogen atom on O(1) forms a hydrogen bond to O(2) on the camphorsulphonate anion; the O(1) · · · O(2), O(1)–H(20), and H(20) · · · O(2) lengths are 2·522(10), 0·64(9), and 1·91(9) Å, and the N–O(1) · · · O(2), N–O(1)–H(20), and O(1)–H(20)–O(2) angles are 116·0(6), 102(8), and 161(10)°. All this evidence, taken in conjunction with the known absolute configuration of the camphor moiety,[6-8] establishes the absolute configuration of the (−)-*N*-oxide as being that of the *S*-enantiomorph (I).[14] This assignment was also supported by the results of the refinement incorporating anomalous dispersion and confirms the decision made on the basis of n.m.r. methods.[2]

TABLE 4

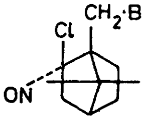
Bond angles (deg.) with estimated standard deviations in parentheses

O(1)–N–C(1)	107·4(6)	C(11)–C(10)–C(19)	115·7(9)
O(1)–N–C(2)	112·2(6)	C(15)–C(10)–C(16)	101·6(6)
O(1)–N–C(4)	105·4(6)	C(15)–C(10)–C(19)	115·3(9)
C(1)–N–C(2)	110·2(8)	C(16)–C(10)–C(19)	119·4(6)
C(1)–N–C(4)	109·2(7)	C(10)–C(11)–O(5)	126·9(7)
C(2)–N–C(4)	112·2(6)	C(10)–C(11)–C(12)	105·9(6)
N–C(2)–C(3)	112·9(9)	C(12)–C(11)–O(5)	127·2(7)
N–C(4)–C(5)	118·5(5)	C(11)–C(12)–C(13)	103·9(8)
N–C(4)–C(9)	116·6(8)	C(11)–C(12)–Br	112·1(5)
C(5)–C(4)–C(9)	124·9(6)	C(13)–C(12)–Br	116·5(7)
C(4)–C(5)–C(6)	113·8(6)	C(12)–C(13)–C(14)	108·8(7)
C(5)–C(6)–C(7)	124·7(8)	C(12)–C(13)–C(16)	99·7(5)
C(6)–C(7)–C(8)	118·4(8)	C(14)–C(13)–C(16)	101·3(5)
C(7)–C(8)–C(9)	121·0(9)	C(13)–C(14)–C(15)	103·9(9)
C(4)–C(9)–C(8)	117·1(1·0)	C(10)–C(15)–C(14)	104·4(9)
O(2)–S–O(3)	111·0(4)	C(10)–C(16)–C(13)	95·1(5)
O(2)–S–O(4)	112·4(4)	C(10)–C(16)–C(17)	111·1(7)
O(2)–S–C(18)	104·8(4)	C(10)–C(16)–C(18)	112·4(5)
O(3)–S–O(4)	112·7(4)	C(13)–C(16)–C(17)	115·2(7)
O(3)–S–C(18)	109·0(4)	C(13)–C(16)–C(18)	114·1(6)
O(4)–S–C(18)	106·4(5)	C(17)–C(16)–C(18)	108·6(7)
C(11)–C(10)–C(15)	102·4(7)	S(4)–C(18)–C(16)	117·8(6)
C(11)–C(10)–C(16)	99·8(5)		

Camphorsulphonate Anion.—While the parent norbornane molecule (III) has C_{2v} symmetry,[15] it has been shown both on the basis of valence force-field calculations and by an examination of the reported *X*-ray results[16] that significant deviations of the carbon skeleton from C_{2v} symmetry occur in derivatives, *e.g.*, in (+)-10-bromo-2-*exo*-chloro-2-nitrosocamphane (IV),[17] in (−)-2-*exo*-bromo-2-nitrocamphane (V),[18] in (+)-3-bromocamphor (VI),[6] in the (+)-3-bromocamphor-9-sulphonate anion in the retusamine salt,[7] and in 1,1′-biapocamphane (VII).[19] Following the nomenclature of ref. 16, the conformation of the camphor ring system can be described as *contra* (−, +). The 'torsion' angles formed by substituents on C(1) and C(4) [chemical convention for camphor, C(10) and C(13) in the crystallographic numbering for the present compound] are given



(III)



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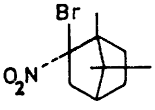

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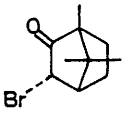

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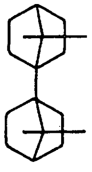
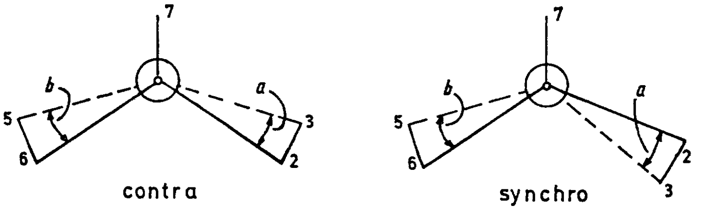


(VII)

TABLE 5

Conformations of the camphor ring in several derivatives following nomenclature of Altona and Sundaralingam.[a] Torsion angles[b] *a* and *b* are given for a series of compounds



	a	*b*	
Present work	−2·9	+2·9	*C*(−, +)
(IV)[c]	−4·7	−0·4	*S*(−, −)[d]
	−1·6	−0·3	*S*(−, −)
(V)[e]	−4·4	+1·3	*C*(−, +)
(VI)[f]	−4·7	+3·4	*C*(−, +)
Camphorsulphonate anion in retusamine[g]	−2·1	+2·0	*C*(−, +)
1,1′-Biapocamphane[h]	−0·8	+1·2	*C*(−, +)

[a] Ref. 16. [b] Angle defined as + if the nearer substituent, *e.g.*, C(6) for *b*, has to be rotated clockwise to eclipse the further substituent, *e.g.*, C(5). [c] Evaluated from co-ordinates in ref. 17; there are two crystallographically independent molecules in the asymmetric unit. [d] The sign of torsion angle *b* is not significantly different from zero, and in ref. 16 the designation for this compound was also given as *C*(−, +). [e] Evaluated from co-ordinates in ref. 18; the co-ordinates presented there corresponded to the wrong absolute configuration for camphor. [f] Ref. 6. [g] Evaluated from co-ordinates in ref. 7. [h] Evaluated from co-ordinates in ref. 19.

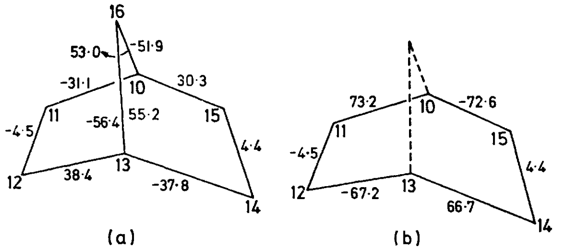


FIGURE 2 Torsion angles in the bicycloheptane ring system of the camphorsulphonate anion: (a) torsion angles within the two five-membered rings of the bicycloheptane system; and (b) torsion angles within the six-membered ring. A positive angle indicates that, when looking along the bond, the nearer substituent has to be rotated clockwise to eclipse the further one

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[14] R. S. Cahn and C. K. Ingold, *J. Chem. Soc.*, 1951, 612; R. S. Cahn, *J. Chem. Educ.*, 1964, **41**, 116.

[15] Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Japan*, 1967, **40**, 1552; J. F. Chiang, C. F. Wilcox, jun., and S. H. Bauer, *J. Amer. Chem. Soc.*, 1968, **90**, 3149; G. Dallinga and L. H. Toneman, *Rec. Trav. chim.*, 1968, **87**, 795.

[16] C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, 1970, **92**, 1995.

[17] G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 1961, 1976.

[18] D. A. Brueckner, T. A. Hamor, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 1962, 799.

[19] R. A. Alden, J. Kraut, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1968, **90**, 74.

and compared with other camphane derivatives in Table 5. The torsion angles along the bonds within the bicycloheptane moiety are given in Figure 2. A more nearly complete listing of torsion angles in camphane and norbornane derivatives is given in ref. 16. The pattern of bond lengths and angles within the camphor moiety agree with those reported for (VI)[6] within the relative accuracies of the two analyses. The very small bridge angle [95·1(5)°] is typical of camphane[6] and norbornane[20] derivatives. This small angle at C(16) is accommodated by an opening out of the other four angles at C(16) which involve either C(10) or C(13).

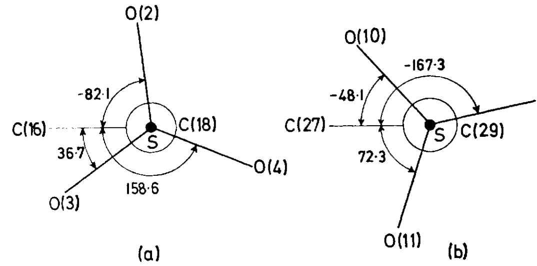

FIGURE 3 (a) The Newman projection looking along the S–C(18) bond in the present structure [atoms numbered according to Table 1; in standard camphor nomenclature, the bond would be S–C(9) and C(16) would be C(7)]; and (b) Newman projection looking along the S–C(29) bond in the camphorsulphonate anion in the retusamine salt (ref. 7) [C(27) and C(29) would be C(7) and C(9) in the standard nomenclature]

The mean S–O length in the sulphonate group is 1·452(7) Å, which agrees well with the values reported in β-sulphanilamide [1·451(2) Å],[21] in methanesulphonanilide [1·434(2) Å],[22] and in sulphathiazole II 1·440(2) Å].[23] The three bond angles at S involving C(18) are slightly smaller (mean 106·7°) than the three O–S–O angles (mean 112·0°). The Newman projection along S–C(18) is shown in Figure 3(a), which also shows that C(16) is closest to O(3); of the three C(18)–S–O angles, that involving O(3) is much larger [109·0(4)°] than the other two. A somewhat similar effect is seen in the same anion in the retusamine structure,[7] where the C(9)–S–O(9), C(9)–S–O(10), and C(9)–S–O(11) angles are 104·3, 107·0, and 107·9°. Figure 3(b) shows the Newman projection along S–C(9) [C(29) in ref. 7], and also shows that C(7) [C(27) in ref. 7] is quite close to both O(10) and O(11), but almost completely *trans* with respect to O(9). There is also evidence from the structure of sulphathiazole II,[23] that intramolecular effects [in that case an S · · · O intramolecular contact of 2·898(3) Å] can cause variations in the N–S–O bond angles.

The Aniline N-*Oxide Cation*.—While some of the bond angles around nitrogen are within a few degrees of the tetrahedral value, there appears to be no obvious pattern to the deviations. The N–O bond length [1·409(10) Å] can be compared with that reported for trimethylamine oxide[24] [1·388(5); 1·404 Å after correction for thermal libration] and with that found in trimethylamine oxide hydrochloride[13] [1·425(11); 1·438 Å corrected[24]]. While the effect of thermal motion on the bond lengths involving nitrogen in the present structure is predictably much less than that in the pseudo-spherical trimethylamine oxide moieties, the question of the exact applicability of the assumptions inherent in making the bond-length corrections renders a close comparison among the N–O lengths in the three compounds of dubious value.

The N–O length[25] in pyridine *N*-oxide hydrochloride [1·37(3) Å] is considerably longer than those reported in 4,4′-*trans*-azopyridine *N*-oxide [1·283(11) Å],[26] 4-nitropyridine *N*-oxide [1·260 Å],[27] 8-hydroxyquinoline *N*-oxide [1·333(2) Å],[28] and 2-hydroxymethylpyridine *N*-oxide [1·332 Å].[28] In any event, the amine *N*-oxide lengths, whether protonated or not, are much longer than the lengths in nitroso-compounds, *e.g.*, 1·264(4) Å in nitrosobenzene,[29] or in nitroxides, *e.g.*, 1·291(7) Å in 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl.[30]

The N–C bond lengths in the present structure (mean 1·503 Å) are somewhat longer than the uncorrected values reported[24] for trimethylamine oxide (mean 1·477 Å), although the agreement with these results corrected for libration is better (1·494 Å). The Newman projection along N–C(4) (Figure 4) shows that O(1) nearly eclipses the C(4)–C(5) bond in the aromatic ring, while the greater steric bulk of the methyl and ethyl substituents force a much greater torsion angle with the C(4)–C(9) bond. The nitrogen atom lies in the plane of the phenyl ring (Table 6).

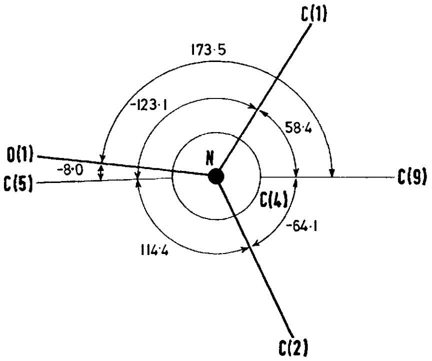

FIGURE 4 Newman projection along the N–C(4) bond in the *N*-oxide cation

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[20] A. C. MacDonald and J. Trotter, *Acta Cryst.*, 1965, **19**, 456; 1965, **18**, 243; R. Destro, G. Filippini, C. M. Gramaccioli, and M. Simonetta, *Tetrahedron Letters*, 1969, 3223.

[21] A. M. O'Connell and E. N. Maslen, *Acta Cryst.*, 1967, **22**, 134.

[22] H. P. Klug, *Acta Cryst.*, 1968, **B24**, 792.

[23] G. J. Kruger and G. Gafner, *Acta Cryst.*, 1971, **B27**, 326.

[24] A. Caron, G. J. Palenik, E. Goldish, and J. Donohue, *Acta Cryst.*, 1964, **17**, 102.

[25] G. Tsoucaris, *Acta Cryst.*, 1961, **14**, 914.

[26] E. L. Eichhorn, *Acta Cryst.*, 1959, **12**, 746.

[27] E. L. Eichhorn, *Acta Cryst.*, 1956, **9**, 787.

[28] R. Desiderato and J. C. Terry, *Tetrahedron Letters*, 1970, 3203.

[29] D. A. Dieterich, I. C. Paul, and D. Y. Curtin, *Chem. Comm.*, 1970, 1710.

[30] L. J. Berliner, *Acta Cryst.*, 1970, **B26**, 1198.

Molecular Packing.—Some short intermolecular contacts are listed in Table 7. A stereoscopic view of the molecular packing is shown in Figure 5. Apart from the hydrogen bond between O(1) in the cation and O(2) in the anion discussed previously, the closest contact is one of 3·17 Å between O(1) and the carbonyl oxygen related by the screw axis. While the N(1)–O(1) · · · O(5) angle [144·3(4)°] might permit hydrogen bonding, there is no doubt that the only available hydrogen atom on O(1) is hydrogen bonded to O(2). There is also a contact of 3·22 Å between C(12) and O(4) in a molecule related by unit translation along *b* (at $x, -1 + y, z$): C(13)–C(12) · · · O(4) is 102·6(6)° and C(11)–C(12) · · · O(4) is 124·5(5)°, so the geometry permits a short C–H · · · O contact. The arguments as to whether such a contact represents a hydrogen bond are given in refs. 31 and 32. The shortest contact between cation and anion, other than the hydrogen bond, is 3·71 Å between C(1) and O(3).

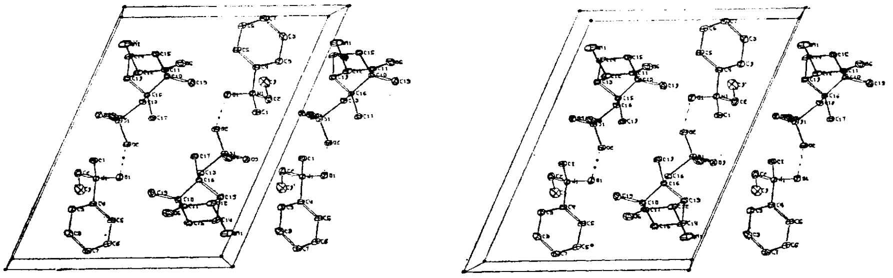

FIGURE 5 A stereoscopic view of the molecular packing

TABLE 6

Details of some best planes with distances (Å) of relevant atoms from the planes given in square brackets

Plane (1): C(4)—(9)
[N −0·012, C(4) 0·006, C(5) −0·014, C(6) 0·016, C(7) 0·005, C(8) −0·018, C(9) 0·008]

Plane 2: N, C(4)—(9)
[N −0·003, C(4) 0·010, C(5) −0·012, C(6) 0·015, C(7) 0·002, C(8) −0·019, C(9) 0·011]

Plane (3): C(10)—(12), O(5)
[C(10) −0·001, C(11) 0·004, C(12) −0·001, O(5) −0·001]

Plane (4): C(10)—(13)
[C(10) 0·016, C(11) −0·029, C(12) 0·026, C(13) −0·014, C(16) 0·874, O(5) −0·107]

Plane (5): C(10), C(13)—(15)
[C(10) 0·013, C(13) −0·012, C(14) 0·030, C(15) −0·031, C(16) 0·853]

Plane (6): C(11), C(12), C(14), C(15)
[C(10) 0·895, C(11) 0·003, C(12) −0·002, C(13) 0·797, C(14) 0·003, C(15) −0·003, O(5) −0·584]

Plane	1	2	3	4	5	6
χ^2	6·9	7·7	0·3	26·4	19·0	0·4
P *	*ca.* 0·10	0·10	0·50	<0·005	<0·005	0·50

* Probability that the deviations from the plane follow a normal distribution.

TABLE 7

Some intermolecular contacts <4 Å

O(5) · · · C(7$^{\text{I}}$)	3·27	O(4) · · · C(17$^{\text{III}}$)	3·63
O(2) · · · C(17$^{\text{II}}$)	3·68	O(4) · · · C(12$^{\text{III}}$)	3·22
O(2) · · · C(19$^{\text{II}}$)	3·53	O(4) · · · C(1$^{\text{III}}$)	3·46
O(1) · · · O(5$^{\text{II}}$)	3·17	C(9) · · · O(3$^{\text{IV}}$)	3·41
C(19) · · · C(5$^{\text{II}}$)	3·63	C(2) · · · O(4$^{\text{IV}}$)	3·39
C(5) · · · O(5$^{\text{II}}$)	3·53	C(1) · · · O(3$^{\text{IV}}$)	3·32

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $1 + x, y, z$
II $1 - x, \frac{1}{2} + y, 1 - z$
III $x, 1 + y, z$
IV $1 - x, -\frac{1}{2} + y, 2 - z$

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[1/1195 *Received, 12th July,* 1971]

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[31] J. Donohue in 'Structural Chemistry and Molecular Biology,' ed. A. Rich and N. Davidson, Freeman, San Francisco, 1968, pp. 443—465.

[32] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968, pp. 182—183.