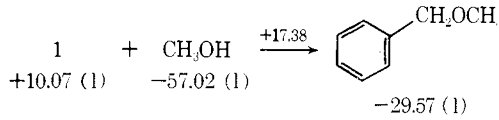
methyl ether was calculated from its boiling point using Trouton's rule as ~9.3 kcal mol^{-1}.

Alternatively, by the Laidler process[18] using for benzocyclopropene $6E(C_b–C_b) + 4E(C_b–H) + 2E(C_b–C) + 2E(C–H)_s$, one obtains $\Delta H_f(g) = +19.46$ kcal mol^{-1}. Similarly, benzyl methyl ether with $6E(C_b–C) + 5E(C_b–H) + 1(C_b–C) + 2E(C–H)_s{}^\circ + 2E(C–O) + 3E(C–H)_p{}^\circ$ yields $\Delta H_f(g) = -19.79$ kcal mol^{-1}.

Thus, for the unstrained model, we can calculate a heat of reaction in solution of +17.38 kcal mol^{-1} by Franklin's method or +17.47 by the Laidler method. Since the observed reaction heat is 51.1 ± 0.2 kcal mol^{-1}, the disparity must be due to the strain present in the system. *This strain is apparently 68 kcal* mol^{-1}! This value is substantially greater than the total strain energy of 52.6 kcal mol^{-1} found for cyclopropene[19] and is comparable to the total strain energy of the bicyclobutane system for which a strain of 68.2 kcal mol^{-1} was found for 1,3-dimethylbicyclo[1.1.0]butane.[20] This high strain energy doubtless accounts for the extremely high reactivity of this compound.



In a similar manner the heat of methanolysis of 2 was determined, and the data are shown in Table II.

Table II. Enthalpy Change for the Reaction 2 (solid) + CH_3OH (liquid) → ether (solution)

Run	Naphtho[*b*]-cyclopropene, g	ΔH, kcal mol^{-1}
1	0.2227	−47.55
2	0.1926	−47.32

By the Laidler scheme, the gas-phase heat of formation of 2 is +36.23 kcal mol^{-1} and −13.14 for the methanolysis product. Assuming a heat of vaporization of 18 kcal mol^{-1} for 2 and 12 kcal mol^{-1} for the ether, the calculated heat of reaction is +13.65 kcal mol^{-1}. Correcting the observed heat of reaction (47.43 kcal mol^{-1}) for the heat of solution of 2 (assumed to be 4–5 kcal mol^{-1}) and the heat of solution of the ether (about 0.7 kcal mol^{-1}) gives the estimated heat of reaction of all components in the liquid phase as −52 to −53 kcal mol^{-1}. This results in a strain energy of 65–67 kcal mol^{-1}.

It was of interest to compare this value with one obtained from more reliable combustion data. Five determinations of the heat of combustion of 2 yielded a value of $\Delta H_c{}^\circ = -1393.8 \pm 0.2$ kcal mol^{-1}. The derived heat of formation of solid 2 is then +86.0 ± 0.2 kcal mol^{-1} and the heat of formation of gaseous 2 becomes[21] +104 kcal mol^{-1}. Comparing this with the value of 36.2 kcal mol^{-1} predicted from the Laidler scheme yields a strain energy of 67.8 kcal mol^{-1}, in good agreement with the value obtained from the methanolysis of 2 and not appreciably different from that found for **1**.

Finally, it should be noted that the thermal data provide information regarding the difference between the real substance and a model. Such differences are often called strain energies or resonance energies, depending on the sign. In the present case where there is clearly some strain, and the aromatic system is deformed, it would not be reasonable to ascribe the effect exclusively to loss of strain or resonance energy. The strain energy of **1** is 68 kcal mol^{-1} if the resonance energy is the same as that of benzene, and, similarly, the strain energy of **2** is 67.8 kcal mol^{-1}, if the resonance energy is the same as that of naphthalene.

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Supplementary Material Available. A listing of structure factor amplitudes, positional parameters, and temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-7878.

[22] Alfred P. Sloan Foundation Fellow, 1973–1975.

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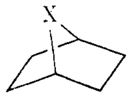
[21] The heat of vaporization of 2 was estimated as 18 kcal mol^{-1}, similar to that of naphthalene.

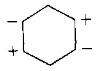
Photoelectron Spectrum of 7-Thiabicyclo[2.2.1]heptane

Sir:

We have recently found that the highest occupied level, which is the oxygen lone pair, of both tetrahydrofuran and 7-oxabicyclo[2.2.1]heptane (**1**) has the same ionization potential (IP = 9.57 eV).[1] This, together with the lack of appreciable interaction between the n_O and π_{CC} levels in 7-oxabicyclo[2.2.1]hept-2-ene, leads to the conclusion that the n_O orbital of **1** is unusually localized. Very recently Hoffmann, *et al.*, have suggested that the highest occupied σ orbital in boat cyclohexane has the symmetry shown in **2**.[2] This σ level is thus unable to interact with the n_O level in **1**,



1, X = O
3, X = S



2

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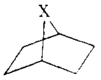
which explains the unexpected stabilization of the lone-pair level in **1**.

In order to investigate this problem further and as a part of our study of the bonding of divalent sulfur compounds,[3-6] we would like to report our results on the high-resolution photoelectron spectra (pes)[7] of 7-thiabicyclo[2.2.1]heptane (**3**) and dimethyl sulfide for comparison.

The first band of the spectrum of **3** is well separated from the others—five complex bands with maxima around 11.0, 12.5, 13.7, 15.5, and 16.8 eV—and this band is quite sharp with a well-resolved vibrational structure, similar to the first band of dimethyl sulfide; see Figure 1. The photoelectron data for **1**, **3**, and related compounds are collected in Table I.

Table I. First IP (eV)[a] of Ethers and Thioethers

X	$(CH_3)_2X$	$(i\text{-}C_3H_7)_2X$		
O	v 10.04[b]	9.20–9.25[c]	9.57[d]	9.57[d]
S	a 8.57			8.28
	v 8.70[e]	8.26[f]	8.40[g]	8.43

[a] Adiabatic (a) ±0.04 eV; vertical (v) ±0.02 eV. [b] From S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, 281 (1972). [c] Estimated, see ref 2 and B. J. Cocksey, J. H. D. Eland, and C. J. Danby, *J. Chem. Soc. B*, 790 (1971). [d] From ref 1. [e] Previous photoelectron determinations gave 8.65,[4] 8.71,[b] and 8.67 (see footnote *f*). [f] From H. Bock and G. Wagner, *Angew. Chem., Int. Ed. Engl.*, **11**, 150 (1972). [g] From H. Schmidt and A. Schweig, *Tetrahedron Lett.*, 1437 (1973).

The three vibrations excited in the first IP of dimethyl sulfide are assigned as follows. The 990-cm^{-1} interval arises from excitation of the totally symmetric CH_3 rocking mode, $\nu_1 = 1027$ cm^{-1} in the neutral molecule.[10] The 660-cm^{-1} spacing corresponds to the symmetric C–S stretching, $\nu_3 = 692$ cm^{-1},[10] and the 305-cm^{-1} spacing corresponds to the CSC bending, $\nu_2 = 282$ cm^{-1} in the neutral molecule.[10] The frequencies observed in the ion, which are ±40 cm^{-1}, do not differ significantly from those of the neutral molecule, reflecting the essentially nonbonding character of the highest occupied molecular orbital in dimethyl sulfide. The vibrational spacings for **3** are 1150, 790, and 340 cm^{-1} and the first two can be compared to the frequencies of 1070–1140 and 860–885 cm^{-1} reported for the neutral molecule in solution.[11a] These data and the sharpness of this first IP suggest that the sulfur lone-pair (n_S) level in **3** is mainly nonbonding as well.

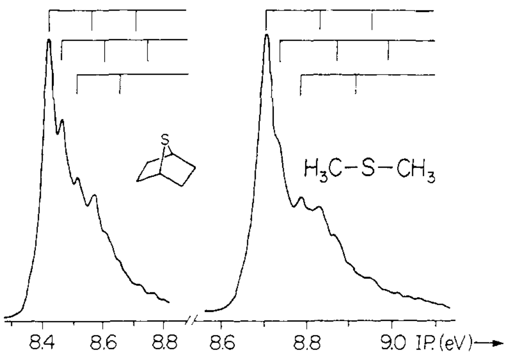


Figure 1. First photoelectron band of **3** and dimethyl sulfide.

Simple deductions based on the inductive effects of alkyl groups[11b] lead to a prediction that the n_S level in **3** should be destabilized relative to the n_S level in tetrahydrothiophene. However, these two compounds have, within experimental error, the same first IP. Also, one would expect, from these simple arguments, that the n_S IP's for diisopropyl sulfide and **3** should be about the same. But the n_S level in diisopropyl sulfide is destabilized by 0.17 eV relative to **3**. CNDO/2 calculations[12] including d orbitals on sulfur confirm that the explanation advanced by Hoffmann, *et al.*, for the corresponding ethers[2] also holds for the thioethers; see Table II. When the methylene group in norbornane is replaced by the sulfur atom in **3**, the a_1 and b_1 norbornane levels are stabilized by ~1.4 and ~1.2 eV since they acquire appreciable sulfur character. But the energy of the a_2 orbital **2** remains essentially the same because the interaction between the n_S level of **3** and the σ level **2** is symmetry forbidden.[13] This is not the case for diisopropyl sulfide where the n_S level is destabilized by interaction with the highest occupied σ level. The sulfur atom in **3** does have d orbitals of the correct symmetry to interact with a σ level of type **2**, but the calculations and the experimental IP's indicate that this interaction is small. This is unlike ethylene sulfide where d orbital participation is important.[5]

Table II. CNDO/2 Calculations on Norbornane and **3**[a]

Norbornane[b]	**3**[c]
	$-11.69\,(b_1)$[d]
$-13.28\,(a_2)$	$-13.02\,(a_1)$
$-14.45\,(a_1)$	$-13.03\,(b_2)$
$-14.71\,(b_2)$	$-13.49\,(a_2)$

[a] Energy levels are given in eV. [b] Geometry from J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968). [c] Geometry of norbornane, with $r_{CS} = 1.82$ Å; this leads to a CSC angle of *ca.* 79°. [d] Localized to 93% on the sulfur atom.

The orbitals of the dialkyl sulfides can be described in terms of the Walsh-type "AH_2" diagram[14] which yields the result that the energy of the b_1 level, that is the sulfur lone pair, should be independent of the CSC angle.[15] This indeed appears to be the case. The CSC angles in the series **3**, tetrahydrothiophene, and

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pentamethylene sulfide are approximately 80, 92, and 100°, respectively.[16] However, all three compounds have essentially the same IP for the b_1 level—**3** (8.43 eV), tetrahydrothiophene (8.40 eV),[17] and pentamethylene sulfide (8.45 eV).[18]

Acknowledgment. We are grateful to the National Research Council of Canada for financial grants, to Professor C. A. McDowell for advice and encouragement, to Professor R. Hoffmann for a preprint of ref 2, and to Professor E. Block for a generous sample of **3**.

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Cholesteric Liquid Crystal Induced Circular Dichroism (LCICD). VII. LCICD of Achiral Solutes in Lyotropic Cholesteric Mesophases

Sir:

We have reported previously that achiral molecules dissolved in thermotropic cholesteric liquid crystals display extrinsic circular dichroism.[1-4] The sign of the liquid crystal induced circular dichroism (LCICD) was found to be dependent on the chirality of the cholesteric helix,[1] preferred orientation of the solute electric transition dipoles,[2,5] the position of λ_0 of the cholesteric pitch band relative to the wavelength of absorption,[3] and the cholesteric matrix.[3] LCICD intensity, on the other hand, has been observed to be a function of the pitch of the helical cholesteric matrix, temperature, and texture.

The origin of the cholesteric liquid crystal induced circular dichroism is attributed to the following: (a) the helical organization of the solute[5] and (b) the exposure of the solute to the chiral organization of liquid crystal molecules.

Recently Sackmann[5,6] and Holzwarth[7,8] have been able to predict the LCICD behavior for both solutes and the cholesteric matrix, respectively. This was done by extending the theory of electromagnetic radiation in nonabsorbing cholesteric liquid crystals to the absorbing case by adding a frequency-dependent complex contribution to the spiralling dielectric tensor of the liquid crystal. In these studies LCICD is attributed to the helical arrangement of molecules in the cholesteric liquid crystal (mechanism a). LCICD has been found experimentally to be proportional to the linear dichroism consistent with theory.[5,6,8] Contribution from mechanism b to LCICD which does not require a helical ordering of the solute but electronic and/or magnetic interactions between solute and matrix molecules[9] has not been clearly established.

Certain synthetic polypeptides, *e.g.*, poly(γ-benzyl-L-glutamate) (PBLG), are known to exist in an α-helical conformation in a variety of solvents.[10] In these systems extrinsic circular dichroism has been observed within the electronic transitions of certain dyes,[11,12] such as Acridine Orange, complexed to isotropically oriented polypeptide molecules in an α-helical conformation. Concentrated solutions of these polypeptides, in helix supporting solvents, readily form birefringent lyotropic cholesteric liquid crystalline mesophases, where the helical polypeptide is analogous to the cholesteryl derivative in thermotropic cholesteric systems.[13,14]

In this communication we wish to report that achiral molecules, such as anthracene and pyrene, which do not exhibit induced circular dichroism in dilute or concentrated isotropic solutions of PBLG, do indeed exhibit LCICD in the anisotropic birefringent lyotropic cholesteric mesophases formed by PBLG in helix supporting solvents such as chloroform, methylene chloride, and dioxane.

LCICD has been observed for a number of achiral molecules dissolved in birefringent concentrated solutions of PBLG in helix supporting solvents. We believe this induced effect to be quite general and independent of the chemical structure of the solute in contrast to rigid requirements for solutes that complex to isotropically oriented helical polypeptides.[11,12] The extrinsic CD of the achiral solute is associated with the formation of the birefringent cholesteric mesophase and disappears when the α-helical molecules of PBLG become randomly orientated by means of small changes in concentrated PBLG while the relative concentration of achiral solute, *e.g.*, anthracene, to PBLG is held constant. In other words, the extrinsic CD of anthracene in PBLG–dioxane mixtures is associated only with the lyotropic cholesteric mesophase.

The observed LCICD for anthracene in the lyotropic cholesteric mesophase formed by PBLG in dioxane is distinctly different from that observed in thermotropic cholesteryl mesophases composed of cholesteryl derivatives.[3] Figure 1 presents the LCICD and electronic spectra of anthracene dissolved in thermotropic and lyotropic cholesteric mesophases. The LCICD spectrum of anthracene between 300 and 400 nm in PBLG–dioxane (18:82 wt %) shows CD bands of a single sign which follow its absorption spectrum quite closely. The CD for the pitch band and anthracene absorption bands are both of negative sign. The chirality of the cholesteric helix in dioxane is then left-handed, *i.e.* of opposite chirality to the helicity of the polypeptide.[15,16] The

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