$PhNCO^+$ and PhCN. We are continuing efforts to delineate the scope of retro-1,3-dipolar cycloaddition reaction induced by electron impact.

Experimental Section

The preparation of the cycloadducts **6**, **7**,[4] and **8**[7] was previously described. The mass spectra were determined with Hitachi RMU-6D mass spectrometer at the ionization voltage 70-eV. The temperature of the sample heater and the ionization chamber was 100 and 250°, respectively.

Registry No.—**1**, 1137-96-8; **3**, 7148-07-4; **4**, 1125-99-1; **6**, 29068-11-9; **7**, 16361-46-9; **8**, 29348-00-3.

Conjugative and Steric Factors Affecting the Conformational Preference of Some Aromatic Sulfides

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We have had for some time evidence that the conformational preference of diphenyl sulfides and analogs could be detected by nmr, based on the fact that the diamagnetic shielding[1] of one ring on the ortho positions of the adjacent nucleus is a function of the molecular conformation.

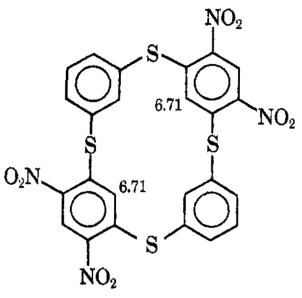
As is already well known,[2] an interesting property of the aromatic sulfides arises from the fact that unshared electrons of the bridged heteroatom may develop a resonance interaction with the π electrons of the aromatic ring.[2]

The intensity of this resonance effect and the extent to which it would affect the conformational preference of these molecules seemed to us an interesting subject of investigation. This paper is concerned with the results obtained in the case of some open-chain and cyclic aromatic sulfides bearing electron-attracting groups (nitro) eventually capable of inducing conformational preferences in these molecules.

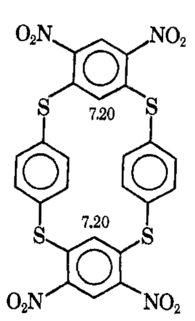
Results and Discussion

The nmr spectra of the two novel cyclic sulfides I and II show that the protons evaluated resonate at somewhat higher field with respect to the corresponding proton in compound III (chemical shift values in parts per million). This suggests that, due to the specific conformation assumed by the cyclic structures, the protons concerned experience the diamagnetic shielding of the adjacent aromatic rings.

Furthermore, comparatively higher shieldings are found for pertinent protons in the open-chain aromatic sulfides IV–VII for which, contrary to the case of cyclic molecules I and II, there are no steric restraints posed on the possible molecular conformations (see below).



I



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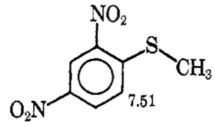
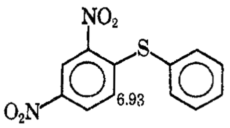
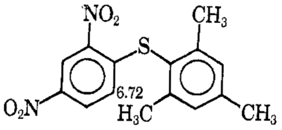


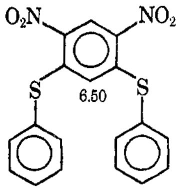
III



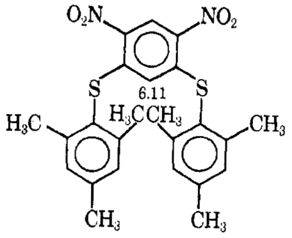
IV



V

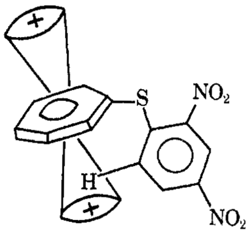


VI



VII

A satisfactory rationalization of these data is obtained considering that, due to the proximity of the aromatic rings in these molecules, the shielding of the ring current[1] of the adjacent nucleus on the ortho positions of the other ring is a function of the molecular conformation. In aromatic sulfides the possibility arises for the unshared electrons of the bridged heteroatom to develop a resonance interaction with the π electrons of the aromatic ring.[2] Here in particular, because of the concerted effect of the two strong electron-attracting groups, a partial bonding arises between π electrons localized on the bridgehead carbon atoms and the unshared electron pairs of the sulfur atom. The percentage of double bond character induced in the C_{Ar}–S bond is here high enough to cause the aromatic ring bearing the two nitro groups to lie in the C_{Ar}–S–C_{Ar} plane. Steric repulsion forces the adjacent ring out of this plane, so that the molecule assumes conformation VIII, where the ortho aromatic hydrogen lies below the



VIII

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[1] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

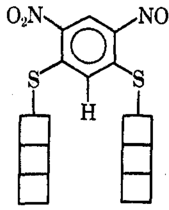
[2] C. C. Price and S. Oae in "Sulphur Bonding," Ronald Press, New York, N. Y., 1962, and references cited therein.

adjacent ring and experiences its diamagnetic shielding.[3]

The experimental nmr shieldings have been computed as the differences between the chemical shifts of each compound and that of compound III.

A theoretical shielding of about 1.0 ppm is calculated[1] for the aromatic proton lying below the adjacent ring (form VIII) in diphenyl sulfide. The agreement is better for compound V ($\Delta = 0.79$ ppm) than IV ($\Delta = 0.58$ ppm) indicating that, if the adjacent ring carries ortho substituents, form VIII receives further stabilization.

In compounds VI and VII the protons under consideration lie between two adjacent phenyl rings, and, if a conformation of type IX is present, the shielding experienced should be nearly doubled with respect to compounds IV and V.

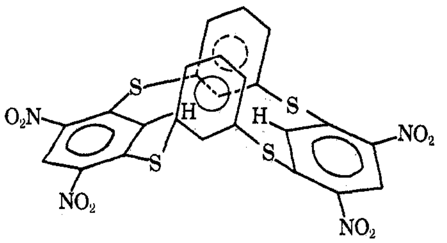


IX

The actual shieldings ($\Delta = 1.01$ and 1.40 ppm, respectively) confirm that conformation IX is preferred in these cases, the preference being stronger for compound VII.

The lower shieldings observed for the cyclic sulfides I and II have a steric origin, we believe. In these molecules, as shown by inspection of molecular models, the cyclic structure puts steric restraints to the existence of conformations of type VIII and IX, and the inner protons are forced somewhat outside the area of maximum shielding.

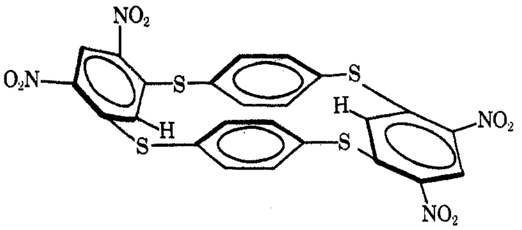
Compound I is thought to exist in a form (X) for which a sensible shielding is still predictable. A similar conformation has been found in solid state[4] for an isostructural cyclic hydrocarbon.



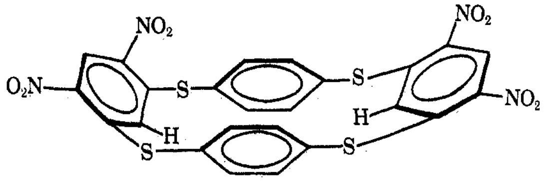
X

Molecular models show two structures (XIa and XIb) as equally plausible in the case of compound II.

In both forms the inner protons appear little shielded, in agreement with the experimental findings. Our results therefore show that, due to the presence of the nitro groups, a strong conjugation develops between the sulfur atom and the aromatic ring bearing the nitro groups in compounds IV–VII. The conjugation energy is strong enough to cause the internal rotation to become thermodynamically (but not kinetically) restricted, so that forms VIII and IX become preferred.



XIa



XIb

Steric factors, however, come into action for cyclic sulfides I and II, which prevent these molecules from assuming conformations of the former type.

Experimental Section

Compound I was obtained by refluxing for 1 hr very dilute ethanol solutions (20:1) of 1,3-benzenedithiol (1.7 g) with NaOH (0.9 g) and 1,3-dichloro-4,6-dinitrobenzene (2.8 g). The yellow precipitate formed was filtered, washed, and dried (yield 65%). Recrystallization from nitrobenzene afforded a product which did not melt up to 350°. *Anal.* Calcd for $C_{24}H_{12}N_4O_8S_4$ (mol wt 612): C, 47.06; H, 1.96; N, 9.16; S, 20.90. Found: C, 47.18; H, 2.20; N, 9.22; S, 21.02. Mass spectrum *m/e* 612 (M^+); nmr (DMSO-d_6, 80°) 9.02 (1 H), 7.69 (4 H), 6.71 ppm (1 H).

Compound II was obtained as above by refluxing 1,4-benzenedithiol (1.7 g), NaOH (0.9 g), and 1,3-dichloro-4,6-dinitrobenzene (2.8 g, yield 70%). The product obtained was infusible up to 350°.

Anal. Calcd for $C_{24}H_{12}N_4O_8S_4$ (mol wt 612): C, 47.06; H, 1.96; S, 20.90. Found: C, 47.24; H, 2.30; N, 9.31; S, 20.93. Mass spectrum *m/e* 612 (M^+); nmr (DMSO-d_6, 80°) 9.04 (1 H), 7.66 (4 H), 7.20 ppm (1 H).

Compounds III, IV, and V were prepared according to the literature.[5] Compound VII was obtained by refluxing 1,3-dichloro-4,6-dinitrobenzene, NaOH, and 1,3,5-trimethyl-2-benzenethiol in ethanol, similarly to the preparation described[6] for compound VI. Data for VII follow.

Anal. Calcd for $C_{24}H_{24}N_2O_4S_2$ (mol wt 468.5): C, 61.52; H, 5.16; N, 5.98; S, 13.69. Found: C, 61.71; H, 6.01; S, 13.90. Nmr ($CDCl_3$, 70°) 9.25 (1 H), 6.73 (4 H), 6.11 (1 H), 2.50 (6 H), 2.07 ppm (12 H); mp 300° (dioxane).

All the nmr measurements were performed with a Varian HA-100 spectrometer (100 MHz).

Registry No.—I, 32730-77-1; II, 32827-45-5; VII, 32827-46-6.

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(3) G. Montaudo, P. Finocchiaro, E. Trivellone, F. Bottino, and P. Maravigna, *Tetrahedron*, **27**, 2125 (1971).

(4) H. Erdtman, S. Hogberg, S. Aghamsson, and B. Nilsson, *Tetrahedron Lett.*, 1679 (1968).

(5) N. M. Cullinane, C. G. Davies, and C. G. I. Davies, *J. Chem. Soc.*, 1435 (1936); G. Leandri and A. Tundo, *Ann. Chim.* (*Rome*), **44**, 261 (1954).

(6) A. Livingstone and J. D. London, *J. Chem. Soc.*, 246 (1937).

A Convenient Synthesis of α-Keto Esters

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Notre Dame, Indiana 46556

Received June 25, 1971

Corey and Seebach[2,3] have described a very convenient method of synthesis of aldehyde and ketone

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(1) From the Ph.D. dissertation of Armando A. Hartmann, University of Notre Dame, Notre Dame, Ind., 1971.

(2) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075 (1965).

(3) D. Seebach, *Synthesis*, **1**, 17 (1969).