

ing, with normal covalent bond lengths of about 1.5–1.6 Å., can lead to the observed high shielding.

$\text{Mn}(\text{CO})_5\text{H}$  crystallizes in the monoclinic space group  $I2/a$  with cell constants  $a = 12.18 \pm 0.02$ ,  $b = 6.35 \pm 0.01$ ,  $c = 19.20 \pm 0.03$  Å., and  $\beta = 93.3 \pm 0.5^\circ$ . There are eight molecules in the unit cell, and the calculated density is 1.75 g/cm<sup>3</sup>. Crystals were grown from the liquid phase by cooling in a stream of cold nitrogen gas, and the sample temperature was held constant at  $-75^\circ$  during the X-ray photography. The intensities of 594 independent reflections were recorded photographically with a Buerger precession camera, using Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å.). The intensities were visually estimated and reduced to structure amplitudes in the usual way. The Mn atom was located from the Patterson function, the carbon and oxygen atoms from an electron density map with the Mn atom subtracted, and the complete structure, including anisotropic temperature factors, but omitting the hydrogen atom, was refined by the least-squares method. The final value of the agreement factor  $R = \sum ||F_{\text{obsd}}| - |F_{\text{calcd}}|| / \sum |F_{\text{obsd}}|$  is 0.045. The standard deviations in the final coordinates are about 0.0015 Å. for Mn and 0.007 Å. for the light atoms. A difference electron density synthesis calculated at this point exhibited a few peaks as high as 0.35 electron/Å.<sup>3</sup>, but there was no convincing indication of the hydrogen atom position.

The molecule has the geometry and dimensions indicated in Fig. 1. The proposed hydrogen position (for which there is no direct evidence) is also indicated. The molecular symmetry departs insignificantly from  $C_{4v}$ , and, if the hydrogen is in the suggested position, the coordination about the manganese atom is octahedral, as suggested by Lohr and Lipscomb for the  $\text{CoH}(\text{CN})_5^{-3}$  ion.  $C_{4v}$  symmetry is not consistent with the interpretations offered by Wilson<sup>7</sup> and by Cotton, Down, and Wilkinson<sup>8</sup> for the gas-phase infrared spectrum of the compound. We consider it unlikely that the configuration in the gas phase is different from that in the solid, and suggest that a reinvestigation of the complex infrared spectra is in order.

The crystal structure is markedly similar to that of  $\text{Mn}_2(\text{CO})_{10}$ .<sup>9</sup> If one breaks the Mn—Mn bond in the latter compound and moves the  $\text{Mn}(\text{CO})_5$  fragments apart by about 3 Å., one obtains very nearly the structure found here. Two  $\text{Mn}(\text{CO})_5\text{H}$  molecules are related by a twofold axis, much as the two halves of the  $\text{Mn}_2(\text{CO})_{10}$  molecule are related, so that the fourfold axes of the molecules are directed toward the crystallographic twofold axis. This implies that the molecules pack so that the hydrogen atoms of the two molecules are probably in contact.

If we assume that the H atoms lie along the  $\text{O}_1\text{—C}_1\text{—Mn}$  line and further assume that, as seems reasonable, the hydrogen atoms are in van der Waals contact at a distance between 2.2 and 2.6 Å., we can calculate that the Mn—H bond length lies between 1.6 and 1.4 Å. We feel that the value of 1.6 is an upper limit, but we can be considerably less certain about the lower value.

The short intermolecular  $\text{H} \cdots \text{H}$  distance is perhaps

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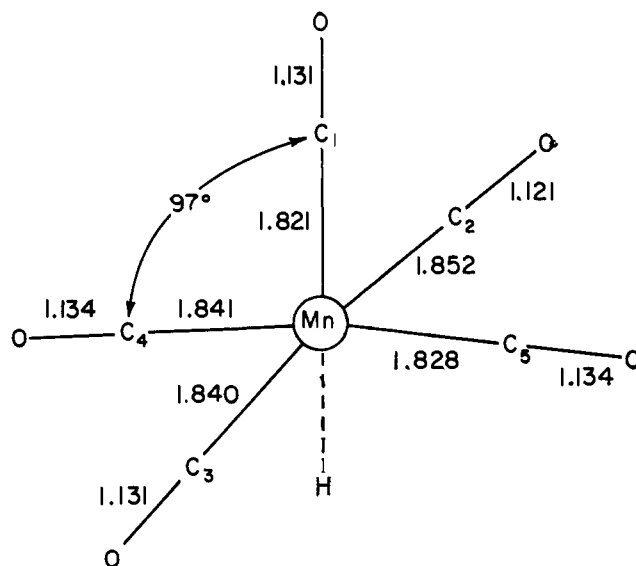


Fig. 1.—Geometry of the  $\text{Mn}(\text{CO})_5\text{H}$  molecule. The position of the hydrogen atom is assumed. The molecule has approximate  $C_{4v}$  symmetry. The estimated standard deviations of the bond lengths are about 0.01 Å. The  $97^\circ$  angle indicated for the angle  $\text{C}_1\text{—Mn—C}_4$  is an average of the four values actually found for  $\text{C}_1\text{—Mn—C}_{\text{base}}$ :  $97.4, 96.9, 95.9,$  and  $96.7^\circ$ , each with an estimated standard deviation of  $0.4^\circ$ .

pertinent with regard to the conclusions drawn from the broad line n.m.r. spectrum of  $\text{Fe}(\text{CO})_4\text{H}_2$ ,<sup>10</sup> where the assumption that the observed second moment was due only to an intramolecular  $\text{H} \cdots \text{H}$  distance forced the authors to derive a low value (1.88 Å.) for this distance and hence a bond length in the neighborhood of 1.1 Å. for the geometries assumed. In view of the result here, we consider it a strong possibility that the observed line width of the n.m.r. spectrum in  $\text{Fe}(\text{CO})_4\text{H}_2$  is due to a sum of contributions from an intramolecular interaction at a distance corresponding to a more reasonable bond length<sup>11,12</sup> and an intermolecular contact of the magnitude inferred here.

In conclusion, we feel that the results of this investigation should encourage further investigations of these compounds by structural chemical techniques. In addition to a neutron diffraction investigation, we are contemplating a broad-line n.m.r. study, which together with an assumption of  $C_{4v}$  symmetry will allow a determination of the Mn—H bond length.

**Acknowledgment.**—We wish to thank Professor W. N. Lipscomb for providing us with a sample of  $\text{Mn}(\text{CO})_5\text{H}$  and to Dr. Kohji Shimaoka for the design of the low temperature apparatus.

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### The Molecular Structure of the Methyl Ester of *o*-Nitrobenzenesulfenic Acid<sup>1</sup>

Sir:

There have been no reports of definitive molecular structures for sulfenic acids or their esters. We

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

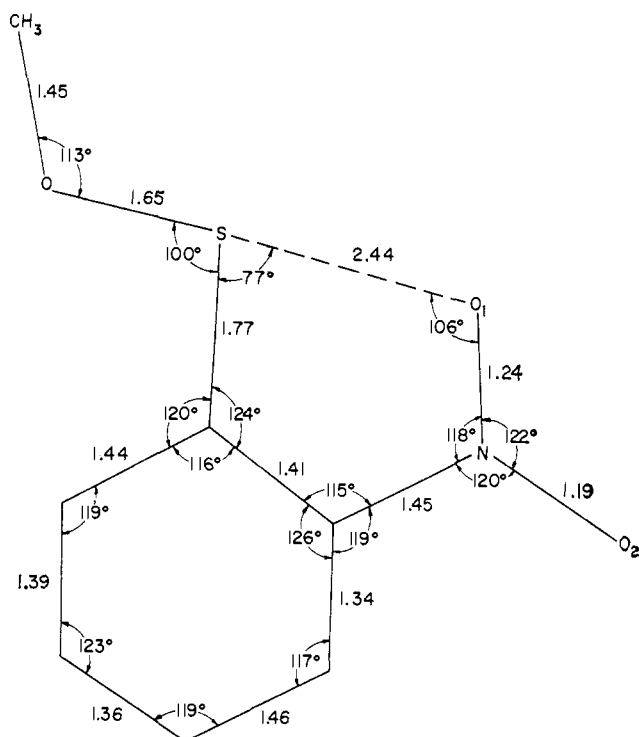


Fig. 1.—Geometry of the molecule of methyl *o*-nitrobenzenesulfonate. The estimated standard deviations in the bond distances are 0.02 Å., except for S—O and C—S, where they are about 0.01. The estimated standard deviations in the bond angles are about 1.5°. With the exception of the methyl group, the molecule is planar. The methyl group is bent out of the plane as far as is consistent with the geometry indicated.

have recently completed an X-ray diffraction investigation of the crystal structure of the methyl ester of *o*-nitrobenzenesulfonic acid. The results should be of interest in view of the speculation which has appeared in the literature regarding the structures of the free acids.<sup>2-4</sup>

The compound crystallizes in the monoclinic space group  $P2_1/n$  with cell dimensions  $a = 14.36 \pm 0.03$ ,  $b = 4.23 \pm 0.01$ ,  $c = 15.33 \pm 0.03$  Å.,  $\beta = 119.1 \pm 0.5^\circ$ . There are four molecules in the unit cell. The details of the crystal structure determination and the molecular packing will be given elsewhere. The bond distances and angles are illustrated in Fig. 1. A section of the electron density in the plane of the molecule (Fig. 2) provides a dramatic illustration of the molecular geometry.

The most striking feature of the molecular structure is the strict planarity of the entire molecule with the exception of the methyl group; associated with this planarity is an extraordinarily short distance (2.44 Å.) between S and one of the oxygen atoms on the nitro group; the sum of the van der Waals radii for S and O is 3.25 Å.<sup>5</sup> The shortness of this distance and the lack of any tendency of the nitro group to rotate out of the plane of the benzene ring are indicative not only of a strong resonance stabilization of the molecule but also of a strong nonbonding attractive interaction between S and O. The O...S—O configuration is

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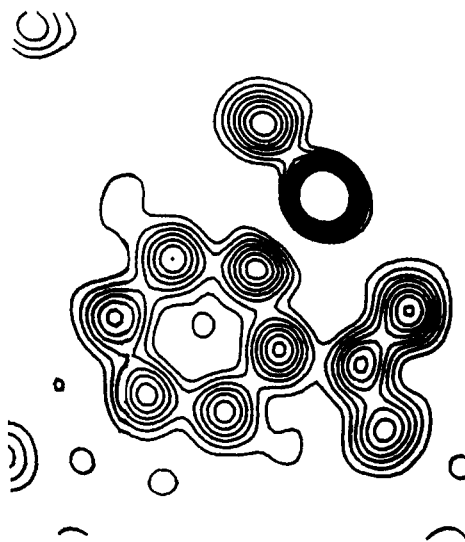


Fig. 2.—Section of the three-dimensional electron density map through the plane of the molecule. Contour interval is 0.625 electron Å.<sup>-3</sup>. The zero contour and contours above 6.25 electrons Å.<sup>-3</sup> are omitted; the sulfur atom thus appears to have a flat top.

almost linear, a favorable situation for sulfur p- and d-orbital participation in the partial bonding. The fact that N—O<sub>1</sub> appears to be somewhat longer than N—O<sub>2</sub> is consistent with a specific interaction between O<sub>1</sub> and S.

Of special interest also is the fact that this investigation has resulted in the first determination of the single bond length between divalent sulfur and oxygen.<sup>6</sup> The value of  $1.648 \pm 0.012$  Å. for an S—O single bond is somewhat shorter than the value 1.70 predicted by the Schomaker—Stevenson rule<sup>7,8</sup> and the value of 1.69 deduced by application of Badger's rule to frequencies deduced from Raman spectra.<sup>9</sup>

There are significant differences between the bond lengths in the benzene ring, but the magnitude of the estimated standard deviations in these bond lengths and the lack of any obvious pattern would make any rationalization of the precise values presumptuous. The mean value is 1.40 Å.

We may conclude that the stability of the *o*-nitro and anthraquinone sulfenic acids is due to a combination of strong resonance stabilization and a specific S...O interaction. We would expect the structure of anthraquinone-1-sulfenic acid to involve a direct S...O interaction, again with a linear O...S—O group, so that there would be no possibility of the internal hydrogen bonding which has been proposed.<sup>2</sup>

**Acknowledgment.**—We wish to thank Dr. Shigeru Oae for suggesting this problem and for providing the crystals.

(6) A value of 1.60 Å. was found for the long S—O bond in potassium ethyl sulfate by J. A. J. Jarvis, *Acta Cryst.*, **6**, 327 (1953). This has been interpreted as being a single S—O bond by S. C. Abrahams, *Quart. Rev. (London)*, **10**, 407 (1956).

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