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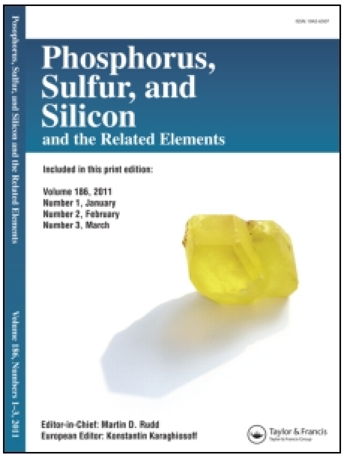

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The Conformation of the Cyclopropylsulfonyl Group

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THE CONFORMATION OF THE CYCLOPROPYLSULFONYL GROUP

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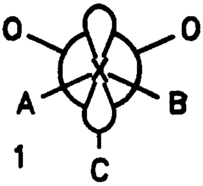
Abstract Single crystal x-ray structures of five cyclopropylsulfonyl compounds all show similar conformations about the (cyclopropyl carbon) - sulfur bond (as in **3**) consistent with cyclopropyl-sulfonyl conjugation.

There is substantial evidence that attachment of a sulfonyl group to an atom (X) bearing non-bonding or π-electrons leads to delocalization, symbolized by $RSO_2{-}X \leftrightarrow R\bar{S}O_2{=}X^+$, and that the preferred conformation of such species is that shown in **1**.



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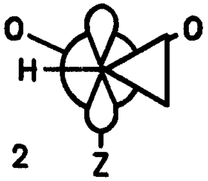

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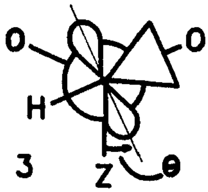
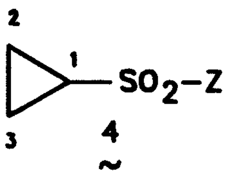


3

There is also good reason for concluding that maximal conjugation of a cyclopropane ring with an electron-withdrawing group occurs in the "bisected" conformation in which the electron-donation from the cyclopropyl ring may be regarded as occurring primarily by overlap with a *p*-orbital on C-1 coplanar with the ring. The simplest combination of these pictures for the sulfonyl and cyclopropyl groups leads to the expectation that the cyclopropylsulfonyl grouping should have the conformation shown in **2**. To examine this point experimentally we have obtained single crystal x-ray structures on compounds **4a** - **4e**, i.e. two sulfonic esters, two sulfones, and one sulfonamide, all with the cyclopropylsulfonyl function. We find that all show the conformation shown in **3** ($\theta = 26 \pm 4°$, see Table I). Such a conformation may be regarded as reflecting a balance of maximization of conjugation consistent with minimization of eclipsing interactions. Evidence supporting cyclopropyl-sulfonyl conjugation was obtained from the cyclopropane ring bond lengths in **4e**, the structure of which was determined at -120°C.

Reported[2] rates of H-D exchange in cyclopropyl isopropyl sulfone and an analogous bridged sulfone are in qualitative accord with the existence of such a conformational effect, but available data do not permit an assessment of the magnitude of its influence on pK_a's or H-D exchange rates.



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a) Z = p-cyanophenoxy
b) Z = p-nitrophenoxy
c) Z = p-chlorophenyl
d) Z = cyclopropyl
e) Z = N-methyl-N-phenylamino

Table I. Values of the dihedral angle θ[a]

Compound (Z)	θ
4a (*p*-cyanophenoxy)	28.3°
4b (*p*-nitrophenoxyl)	29.6°
4c (*p*-chlorophenyl)	27.8°
4d (cyclopropyl)	19.5°
4e (*N*-methyl-*N*-phenylamino)	29.8°
	Average 26.2 ± 4.2°

[a] $\theta = \frac{1}{2}(\alpha + \beta) - 90$ where α is the Z–S–(C-1)–(C-2) and β is the Z–S–(C-1)–(C-3) dihedral angle

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