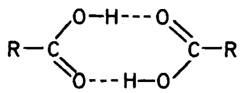
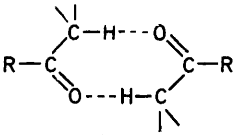
Hydrogen Bonds involving Polar C–H Groups. Part 7.[1] Electron-deficient Cyclohexenones as Analogues of Carboxylic Acid Dimers, and the Crystal and Molecular Structure of 5,5-Dimethyl-3-methylsulphonylcyclohex-2-enone

By **Kin Shing Luk** and **Michael P. Sammes,*** Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong
Richard L. Harlow,* Central Research and Development Department, Experimental Station, E. I. duPont de Nemours and Company, Wilmington, Delaware 19898, U.S.A.

Three 3-sulphonylcyclohex-2-enones have been prepared as potential C–H analogues of carboxylic acid dimers, the molecules being designed to associate as doubly bridged hydrogen-bonded dimers *via* their alkene C–H groups. ^1H N.m.r. and i.r. spectra show no evidence of such an association. The crystal and molecular structure of the title compound has been determined from *X*-ray diffraction data by direct methods and refined to *R* 0.034 for 2 008 independent reflections. The crystals are monoclinic, $a = 10.243(1)$, $b = 8.755(2)$, $c = 11.672(2)$ Å, $\beta = 102.94(1)^\circ$ (at 153 K), space group $P2_1/c$, and $Z = 4$. Although the molecules associate as dimers, the H ··· O distance (2.63 Å) is too long to be described as a hydrogen bond. The association probably arises from dipole–dipole attractions between the polarised C–H groups and the carbonyl oxygen atoms of the two molecules.

As an extension of our earlier investigations into hydrogen bonding by C–H groups,[1,2] we wished to prepare C–H analogues of carboxylic acid dimers (1), such that association of the molecules would take place *via* doubly bridged C–H ··· O hydrogen bonds (2), in place of O–H ··· O bonds. Both in 2-chloro-1,4-benzoquinone (3) [3] (though not in the 2,3-, 2,5-, or 2,6-dichloro-analogues[4]), and in the 4-nitropyridine 1-oxides (4),[5] associations of this type appear to be important in the solid state; also, certain aryl(nitrofuryl)propenones [6] associate into dimers but with the bridges spaced farther apart.


(1)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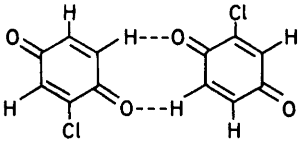
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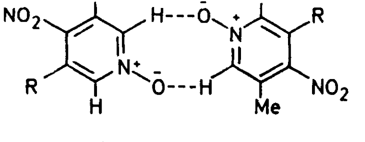
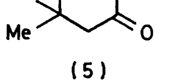
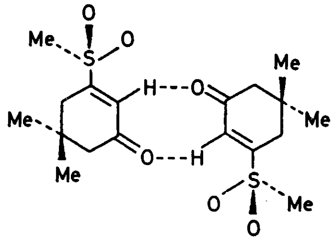

(4) a ; R = H
b ; R = Me

The requirement that the C–H bond α to the carbonyl group in structure (2) be both polar and non-enolisable suggested αβ-unsaturated ketones as models. Further, cyclic structures offered the added advantage that the polar C–H and the ketone groups would be fixed in the correct relative stereochemical relationship; so derivatives (5) of the readily available 5,5-dimethylcyclohexane-1,3-dione (dimedone), having a strongly electron-withdrawing group X, were selected for the initial study.


(5)

a ; X = OH
b ; X = Cl
c ; X = Br
d ; X = NH_2
e ; X = $MeSO_2$
f ; X = $PhSO_2$
g ; X = 4-$MeC_6H_4SO_2$


(5e)

We report the preparation of the sulphones (5e—g), a comparison of the ^1H n.m.r. and i.r. spectra for their alkene C–H groups with those for other derivatives of structure (5), and the crystal and molecular structure of the methyl sulphone (5e).

EXPERIMENTAL

The substituted cyclohexenones (5b) (90%),[7] (5c) (51%),[8] and (5d) (95%),[9] were prepared by published methods. I.r. spectra were recorded on a Perkin-Elmer model 577 spectrophotometer for Nujol mulls, polystyrene being used in calibration. ^1H N.m.r. spectra were run on a Perkin-Elmer R-20 spectrometer for solutions in $CDCl_3$ with Me_4Si as internal reference. The effect of concentration on the chemical shift of H(2) of the sulphone (5e) was determined for solutions in CD_3CN.

Preparation of Sulphones.—*5,5-Dimethyl-3-methylsulphonylcyclohex-2-enone* (5e). The chloro-enone (5b) (0.005 mol) and sodium methanesulphinate (0.01 mol)[10] were heated under reflux in 95% EtOH (20 ml) for 0.5 h. Removal of the solvent followed by recrystallisation of the residue (CCl_4) gave the *methyl sulphone* (5e) (80%), prisms, m.p. 92—93 °C (Found: C, 53.2; H, 6.9; S, 15.6. $C_9H_{14}O_3S$ requires C, 53.4; H, 7.0; S, 15.9%); M^+ 202; $\nu_{max.}$ 3 058, 1 690, 1 620, 1 305, and 1 140 cm^{-1}; δ 6.71 (1 H, t, J 2 Hz), 3.00 (3 H, s), 2.59 (2 H, d, J 2 Hz), 2.36 (2 H, s), and 1.14 (6 H, s). Prepared similarly from the appropriate sodium sulphinates were the phenyl sulphone (5f) (60%), prisms from 95% EtOH, m.p. 81 °C (lit.,[11] 76—81 °C) (Found: C, 63.3; H, 6.2; S, 12.4. Calc. for $C_{14}H_{16}O_3S$: C, 63.6; H, 6.1; S, 12.1%); M^+ 264; $\nu_{max.}$ 3 062, 1 685, 1 309, and 1 148 cm^{-1}; δ 8.1—7.5 (5 H, m), 6.72 (1 H, t, J 2 Hz), 2.39 (2 H, d, J 2 Hz), 2.27 (2 H, s), and 0.95 (6 H, s); and the *tolyl sulphone* (5g) (52%), prisms from 95% EtOH, m.p. 86 °C (Found: C, 64.8; H, 6.5; S, 11.8. $C_{15}H_{18}O_3S$ requires C, 64.7; H, 6.5; S, 11.5%); M^+ 278; $\nu_{max.}$ 3 059, 1 690, 1 659, 1 320, and 1 120 cm^{-1}; δ 7.81 (2 H, d, J 9 Hz), 7.38 (2 H, d, J 9 Hz), 6.68 (1 H, t, J 2 Hz), 2.47 (3 H, s), 2.39 (2 H, d, J 2 Hz), 2.27 (2 H, s), and 0.97 (6 H, s).

TABLE 1

Final positional parameters for sulphone (5e) with estimated standard deviations in parentheses

(*a*) Non-hydrogen atoms

Atom	*x*	*y*	*z*
S	0.135 87(4)	0.280 46(4)	0.275 27(3)
O(1)	−0.002 4(1)	0.328 4(1)	0.248 7(1)
O(2)	0.190 3(1)	0.219 3(1)	0.390 3(1)
O(3)	0.529 2(1)	0.637 3(2)	0.381 4(1)
C(1)	0.231 5(1)	0.442 3(2)	0.251 1(1)
C(2)	0.340 0(1)	0.477 2(2)	0.333 4(1)
C(3)	0.416 6(1)	0.617 8(2)	0.321 5(1)
C(4)	0.346 2(1)	0.731 2(2)	0.232 3(1)
C(5)	0.277 3(1)	0.652 8(2)	0.116 5(1)
C(6)	0.177 1(1)	0.533 9(2)	0.142 2(1)
C(7)	0.158 5(2)	0.146 9(2)	0.169 1(2)
C(8)	0.383 0(1)	0.575 2(2)	0.062 1(1)
C(9)	0.201 6(2)	0.772 2(2)	0.031 4(1)

(*b*) Hydrogen atoms *

Atom	*x*	*y*	*z*
H(2)	0.366(1)	0.421(2)	0.396(1)
H(4A)	0.410(1)	0.806(2)	0.218(1)
H(4B)	0.280(2)	0.779(2)	0.267(1)
H(6A)	0.151(2)	0.468(2)	0.076(1)
H(6B)	0.095(2)	0.583(2)	0.153(1)
H(7A)	0.250(2)	0.125(2)	0.182(2)
H(7B)	0.109(2)	0.067(2)	0.182(2)
H(7C)	0.122(2)	0.194(2)	0.092(2)
H(8A)	0.430(2)	0.490(2)	0.113(2)
H(8B)	0.345(2)	0.529(2)	−0.012(1)
H(8C)	0.448(2)	0.649(2)	0.050(2)
H(9A)	0.260(2)	0.852(2)	0.018(2)
H(9B)	0.160(2)	0.727(2)	−0.043(1)
H(9C)	0.134(2)	0.821(2)	0.061(1)

* Each numbered in accord with the carbon atom to which it is bonded.

Crystal Data for the Sulphone (5e).—$C_9H_{14}O_3S$, M = 202.27, monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$. At 153 K: $a = 10.243(1)$, $b = 8.755(2)$, $c = 11.672(2)$ Å, $\beta = 102.94(1)°$, $U = 1\,020.1$ Å^3, $D_c = 1.317$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 2.8 cm^{-1}.

Crystals were grown by slow evaporation from a CCl_4 solution. A crystal with approximate dimensions of 0.23 × 0.24 × 0.30 mm was mounted on a Syntex P3 diffractometer equipped with a low-temperature apparatus which cooled the crystal to 153 K. The unit-cell dimensions at this temperature were refined from the setting angles of 50 computer-centred reflections in the range $24° < 2\theta < 26°$

Intensity data for 2 344 unique reflections ($4° < 2\theta < 55°$, graphite monochromatised Mo-K_α radiation) were collected by the ω-scan technique. Scans of 1° were used with scan rates ranging from 2.0—5.0° min^{-1} depending upon the number of counts measured in a rapid preliminary scan.

TABLE 2

Bond distances (Å) and angles (°) for sulphone (5e) with estimated standard deviations in parentheses

(*a*) Distances

S–O(1)	1.442(1)	C(5)–C(8)	1.532(2)
S–O(2)	1.437(1)	C(5)–C(9)	1.528(2)
S–C(1)	1.780(1)	C(6)–H(6A)	0.96(1)
S–C(7)	1.756(1)	C(6)–H(6B)	0.98(1)
C(1)–C(2)	1.331(1)	C(7)–H(7A)	0.94(2)
C(1)–C(6)	1.501(1)	C(7)–H(7B)	0.90(2)
C(2)–C(3)	1.483(2)	C(7)–H(7C)	0.99(2)
C(2)–H(2)	0.87(1)	C(8)–H(8A)	1.01(1)
C(3)–O(3)	1.219(1)	C(8)–H(8B)	0.95(1)
C(3)–C(4)	1.501(2)	C(8)–H(8C)	0.96(1)
C(4)–C(5)	1.540(1)	C(9)–H(9A)	0.95(1)
C(4)–H(4A)	0.96(1)	C(9)–H(9B)	0.96(1)
C(4)–H(4B)	0.96(1)	C(9)–H(9C)	0.94(1)
C(5)–C(6)	1.538(1)		

(*b*) Angles

O(1)–S–O(2)	117.8(1)	C(2)–C(3)–O(3)	121.0(1)
O(1)–S–C(1)	106.4(1)	C(2)–C(3)–C(4)	115.6(1)
O(1)–S–C(7)	108.7(1)	O(3)–C(3)–C(4)	123.4(1)
O(2)–S–C(1)	109.4(1)	C(3)–C(4)–C(5)	111.6(1)
O(2)–S–C(7)	109.0(1)	C(4)–C(5)–C(6)	109.0(1)
C(1)–S–C(7)	104.7(1)	C(4)–C(5)–C(8)	109.5(1)
S–C(1)–C(2)	118.0(1)	C(4)–C(5)–C(9)	109.4(1)
S–C(1)–C(6)	116.5(1)	C(6)–C(5)–C(8)	110.2(1)
C(2)–C(1)–C(6)	125.4(1)	C(6)–C(5)–C(9)	109.1(1)
C(1)–C(2)–C(3)	119.8(1)	C(8)–C(5)–C(9)	109.7(1)
C(1)–C(2)–H(2)	121.7(8)	C(1)–C(6)–C(5)	113.0(1)
C(3)–C(2)–H(2)	118.5(8)		

Backgrounds were measured at both ends of the scan with ω displaced 1° from the K_α peak. Intensities were corrected for Lorentz and polarisation effects, but not for absorption (ψ-scans showed no change in intensity).

Solution and Refinement.—The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of the programs supplied by the Enraf-Nonius Corp.[12] The atomic scattering factors were taken from the tabulations of Cromer and Waber;[13a] anomalous dispersion corrections were by Cromer.[13b] In the least-squares refinement, the function minimised was $\Sigma\, w(|F_o| - |F_c|)^2$ with the weights w assigned as $1/\sigma^2(F_o)$. The standard deviations of the observed structure factors $\sigma(F_o)$ were based on counting statistics and an ' ignorance factor ' p of 0.02.[14]

The structure was solved by direct methods. The positions of the hydrogen atoms were determined by Fourier difference techniques. Full matrix least-squares refinement of all positional and thermal parameters (anisotropic for S, O, and C; isotropic for H) using the 2 008 reflections with $F_o^2 > 2\ \sigma(F_o^2)$ converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.034$ and $R_w = [\Sigma w(|F_c| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.038$. The largest peak in the final difference map was located near the sulphur atom, and had a magnitude of 0.36 e Å^{-3}.

The final positional parameters are given in Table 1. Bond distances and angles are listed in Table 2, selected torsion angles in Table 3, intermolecular distances and angles about the atom H(2) in Table 4. Final observed and calculated structure factors, and thermal parameters, are in Supplamentary Publication No. SUP 22762 (18 pp.).*

RESULTS AND DISCUSSION

Description of the Structure.—It appears from the ORTEP drawing presented in the Figure, that molecules of (5e) form dimers about a crystallographic centre of symmetry. However, it seems from the data in Table 4 that the H · · · O′ (2.63 Å) and C · · · O′ (3.448 Å) distances are too long for the interaction to be described as a hydrogen bond. Hydrogen bonds involving *sp* hybridized C–H groups which have been authenticated both by i.r. spectroscopy and by *X*-ray crystallography [15] show H · · · O′ distances in the 2.2—2.4 Å, and C · · · O′ distances in the range 3.2—3.4 Å. Likewise, reported C · · · O′ distances involving sp^3 hybridized C–H groups lie close to 3.1 Å.[16] Although no intermolecular hydrogen bonds involving sp^2 hybridized C–H groups appear to have been fully authenticated, both by spectroscopic and *X*-ray crystallographic measurements,† reported structures in which such interactions are feasible show H · · · O′ and C · · · O′ distances respectively of *ca.* 2.4 Å and in the range 3.1—3.3 Å.[4,5,18] The C–H · · · O′ angle of 157° (Table 4) deviates appreciably from the most favourable value (180°). However, while some genuine C–H · · · O′ hydrogen bonds are essentially linear,[16] others have angles as small as 154 and 162°.[15] Further evidence against the existence of hydrogen bonds in crystals of the sulphone (5e) lies in the observation (Table 5) that the planes of the two H(2)–C(2)–C(3)–O(3) moieties across the centre of symmetry are separated by *ca.* 1 Å. In carboxylic acid dimers the corresponding two groups of four atoms all lie in essentially the same plane.[19]

TABLE 3

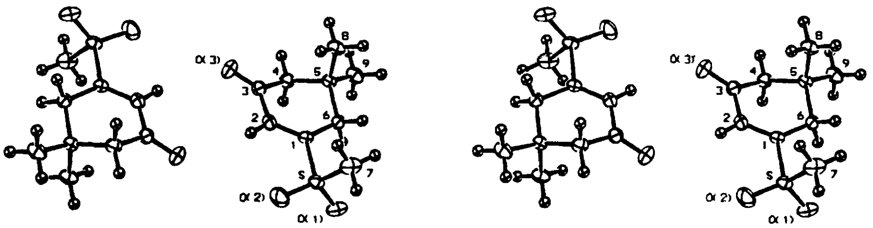
Selected torsion angles (°)

S–C(1)–C(2)–C(3)	−175.2	C(2)–C(3)–C(4)–C(5)	−44.8
S–C(1)–C(2)–H(2)	2.3	C(3)–C(2)–C(1)–C(6)	0.7
S–C(1)–C(6)–C(5)	−169.6	C(3)–C(4)–C(5)–C(6)	58.1
C(1)–C(2)–C(3)–C(4)	14.9	C(3)–C(4)–C(5)–C(8)	−62.6
C(1)–C(2)–C(3)–O(3)	−165.2	C(3)–C(4)–C(5)–C(9)	177.2
C(1)–C(6)–C(5)–C(4)	−42.4	C(4)–C(3)–C(2)–H(2)	−162.7
C(1)–C(6)–C(5)–C(8)	77.8	C(5)–C(4)–C(3)–O(3)	135.3
C(1)–C(6)–C(5)–C(9)	−161.8	C(6)–C(1)–S–O(1)	−43.4
C(2)–C(1)–S–O(1)	132.9	C(6)–C(1)–S–O(2)	−171.6
C(2)–C(1)–S–O(2)	4.6	C(6)–C(1)–S–C(7)	71.6
C(2)–C(1)–S–C(7)	−112.1	C(6)–C(1)–C(2)–H(2)	178.1
C(2)–C(1)–C(6)–C(5)	14.5	O(3)–C(3)–C(2)–H(2)	17.3

TABLE 4

Intermolecular contacts about the atom H(2)

H(2) · · · O(3′)	2.63(1) Å	C(2)–H(2) · · · O(3′)	157(1)°
C(2) · · · O(3′)	3.448(1) Å	C(3)–O(3) · · · H(2′)	131.6(3)°



ORTEP drawing of the sulphone (5e) which shows the relationship between molecules in a given pair

The C(1)–C(2), C(2)–C(3), and C(3)–O(3) distances are normal for an electron-deficient conjugated enone,[3] and differ in a predictable fashion from the corresponding lengths in the enolic form of dimedone (5a) [20] due to the +*M* effect of the enolic oxygen atom in the latter. The ring, however, is found to be in the same ' envelope ' conformation as in structure (5a).[20] The bond lengths and angles about the methylsulphonyl group agree closely with published values for a methyl vinylic sulphone,[21] except for the S–C(1) distance in sulphone (5e) (1.780 Å) which is 0.046 Å longer than that in the analogous compound. However, in a series of aryl alkyl sulphones, we have found C(sp^2)–S bond lengths of 1.783,[2a] 1.763,[2c] and 1.769 Å.[2d]

TABLE 5

Least squares mean plane equation and distances (Å) from the plane for atoms at the potential hydrogen bond site [a]

Atom	*X*	*Y*	*Z*	Distance
O(3) *	4.4242	5.5793	4.3381	0.029(1)
C(3) *	3.4269	5.4090	3.6576	−0.052(1)
C(2) *	2.6109	4.1783	3.7926	0.063(1)
H(2) *	2.7122	3.6888	4.5070	−0.039(16)
O(3′)	3.2051	3.1757	7.0375	−0.990(1)
C(3′)	4.2024	3.3460	7.7180	−0.909(1)
C(2′)	5.0184	4.5767	7.5830	−1.024(1)
H(2′)	4.9171	5.0662	6.8686	−0.922(16)

[a] The equation is of the form: $(0.5839)X + (-0.5465)Y + (-0.6003)Z + (-3.0985) = 0$. *X*, *Y*, and *Z* are orthogonalised co-ordinates in Å. The atoms used in the plane calculation are indicated with an asterisk.

The only other noteworthy close intermolecular contact is that between H(7a) and O(3′), which at 2.53 Å is disappointingly shorter than the H · · · O′ contact of interest. It is possible that O(2), lying almost in the same plane as S–C(1)–C(2)–H(2),‡ and separated from H(2) by only 2.51 Å, sterically inhibits a closer approach

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* For details of the Supplementary Publications scheme, see Notice to Authors No. 7, *J.C.S. Perkin II*, 1979, Index issue.

† In view of the large number of C–H · · · X close approaches recorded in *X*-ray crystallographic papers, we have suggested [1] that claims for hydrogen bonding should be further substantiated by shifts in i.r. and ^{1}H n.m.r. spectra. However a recent paper [17] has revealed little correlation between formation constants for C–H hydrogen bonds, and shifts in ν_{C-H} in i.r. spectra.

‡ See Table 5 for least squares planes: the torsion angle O(2)–S–C(1)–C(2) is only 4.6°.

by O(3′) to H(2). The apparent, though unreal, shortening of the C(2)–H(2) bond, may nevertheless indicate significant polarisation of the bonding electrons in the desired direction.

Spectroscopic Data.—^{1}H N.m.r. spectroscopic data relating to H(2) are given in Table 6. The change in chemical shift for H(2) in the series (5; X = NH_2, OH, Cl, Br, SO_2R) can be accommodated by electronic and anisotropic effects due to the group X without invoking hydrogen bonding. Thus, the corresponding hydrogen atom in divinyl sulphone appears at $\delta(CDCl_3)$ 6.6.[22] Further, a 2.0M solution of the sulphone (5e) in CD_3CN showed no measurable change in chemical shift for H(2) (δ 6.45) when diluted in three steps to 0.15M.*

The i.r. stretching frequencies of the C(2)–H(2) bond in compounds (5), where measurable, were found to be essentially independent of the nature of X, the only observation of note being that the band in the sulphone (5e) was very much more intense than that for the other compounds.

TABLE 6

Chemical shifts (δ) for H(2)($CDCl_3$), and i.r. stretching frequencies (cm^{-1}) for C(2)–H(2) (Nujol) in cyclohexones (5)

Compound	δ	$\nu_{max.}$	Compound	δ	$\nu_{max.}$
(5d)	5.16	*a*	(5e)	6.71	3 058
(5a)	5.47	*a*	(5f)	6.72	3 062
(5b)	6.21	3 062	(5g)	6.68	3 059
(5c)	6.42	3 062			

[a] Hidden by O–H or N–H absorptions.

In conclusion, if we accept the maximum H $\cdots$ O distance for hydrogen bonding to be 2.4 Å,[23] and require spectroscopic evidence for such interactions, it appears that sufficient polarisation of the C(2)–H(2) bond has been achieved to influence the orientation of molecules of the sulphone (5e) in the crystal lattice, but that the interaction between H(2) and O(3′) is better described as a dipole–dipole attraction rather than as a hydrogen bond.

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* The only solvent found suitable for such measurements, due to solubility limitations, was CD_3CN, though we recognise that an interaction between H(2) and the solvent is a possibility.

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