current chemical theory and greatly limits the region where more complex, and correspondingly less visualizable, models need to be used.

This work also has possible implications for molecular mechanics, which is in effect a mathematical formulation of the localized bond model. The arguments presented here suggest that some at least of the problems currently being encountered in parametrizing such treatments may well be due to the current neglect of $\sigma$ conjugation. Attempts to include small ring compounds in such schemes, without reference to the apparently large $\sigma$-aromatic stabilization of three-membered rings, must, for example, greatly distort the treatment of angle strain. Problems

may also arise from the description of rotation about single bonds in terms of 3-fold barriers. The analysis given here suggests that such barriers might be simulated more effectively by a superposition of 1-fold barriers, using a sharper function than a simple cosine function; for example, $\cos \theta |\cos \theta|$. Adoption of such a scheme might well overcome some of the difficulties presented by heteroatoms in such treatments.

# Structure of Meerwein's Ester and Its Benzene Inclusion Compound

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**Abstract:** The structure of Meerwein's ester (**1**) has been established by spectroscopic means (NMR, IR) and by single-crystal X-ray diffraction. In solution and in the solid state, **1** exists as a dienol (**1b**), which is stabilized by conjugate chelation. Crystals of the benzene solvate of **1** are orthorhombic, space group *Pnaa*, $a = 11.867$ (2), $b = 12.667$ (1), and $c = 25.601$ (3) Å, with four stoichiometric benzene molecules per molecule of **1**. The ester molecules are located on crystallographic 2-fold rotation axes and are sheathed in a channel of benzene molecules (Figure 3). In this unusual inclusion compound, it is not clear whether **1** is the host or the guest molecule.

In 1913 Meerwein and Schürmann[2a] described a one-step synthesis (from methyl malonate and formaldehyde) of an ester, since known as "Meerwein's ester" (**1**), that they identified as 1,3,5,7-tetracarbomethoxybicyclo[3.3.1]nonane-2,6-dione (**1a**) and
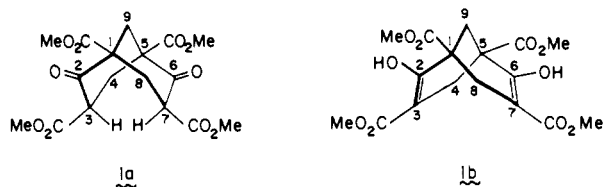


that has proven its versatility as a key intermediate in the synthesis of a wide variety of bicyclo[3.3.1]nonane[3] and adamantane[4,5] derivatives.

The structure (**1a**) assigned to Meerwein's ester has stood unchallenged to this day. We now present conclusive evidence that the ester is in fact completely enolized, both in the solid state

and in solution, and that its structure must therefore be revised to that of 1,3,5,7-tetracarbomethoxybicyclo[3.3.1]nona-2,6-diene-2,6-diol (**1b**). In addition, we describe the structure of the benzene solvate of **1**, whose packing arrangement is unusual for an organic inclusion compound.

## Results and Discussion

**Nuclear Magnetic Resonance Spectra.** The $^1$H NMR spectrum of **1** in CDCl$_3$ features a sharp singlet at $\delta$ 12.14 due to the enolic protons in **1b**. This chemical shift is in excellent agreement with the value of 12.12 ppm observed for the hydroxyl proton in the enol form of a related cyclic $\beta$-keto ester, 2-carbethoxycyclohexanone (**2b**).[6] The presence of the diketo form of Meerwein's
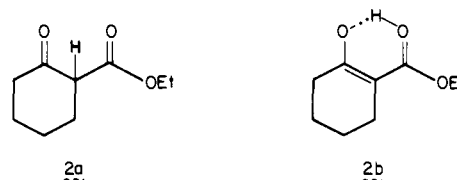


ester (**1a**) would have been revealed by a multiplet centered near 3.2 ppm due to the protons at C-3 and C-7, as observed for the $\alpha$-hydrogen in the keto form of 2-carbethoxycyclohexanone (**2a**).[6] However, no such signal was observed for **1**, even at low temperatures in CD$_2$Cl$_2$ or in methanol.

Furthermore, the signal at 12.14 was found to be insensitive to changes in concentration, suggestive of strong intramolecular hydrogen bonding. The $^1$H NMR evidence thus indicates that

(1) (a) Princeton University. (b) Hoffmann-La Roche Inc.

(2) (a) Meerwein, H.; Schürmann, W. *Justus Liebigs Ann. Chem.* **1913**, *398*, 196. (b) See also: Meerwein, H. *J. Prakt. Chem.* **1922**, *104*, 161. Landa, S.; Kamýček, Z. *Collect. Czech. Chem. Commun.* **1959**, *24*, 1320. Schaefer, J. P.; Honig, L. M. *J. Org. Chem.* **1968**, *33*, 2655.

(3) For reviews, see: Buchanan, G. L. *Top. Carbocyclic Chem.* **1969**, *1*, 199. Zefirov, N. S. *Russ. Chem. Rev. (Engl. Transl.)* **1975**, *44*, 196. Peters, J. A. *Synthesis* **1979**, 321.

(4) For reviews, see: Stetter, H. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 286. Fort, R. C., Jr.; Schleyer, P. v. R. *Chem. Rev.* **1964**, *64*, 277. Fort, R. C., Jr. "Adamantane"; Marcel Dekker: New York, 1976.

(5) Meerwein's ester was the starting material for the first synthesis of an adamantane derivative [Böttger, O. *Ber. Dtsch. Chem. Ges.* **1937**, *70*, 314] and for the first synthesis of adamantane itself [Prelog, V.; Seiwerth, R. *Ber. Dtsch. Chem. Ges.* **1941**, *74*, 1644].

(6) Rhoads, S. J. *J. Org. Chem.* **1966**, *31*, 171. See also: Forsén, S.; Merényi, F.; Nilsson, M. *Acta Chem. Scand.* **1964**, *18*, 1208.

*Meerwein's Ester and Its Benzene Inclusion Compound*
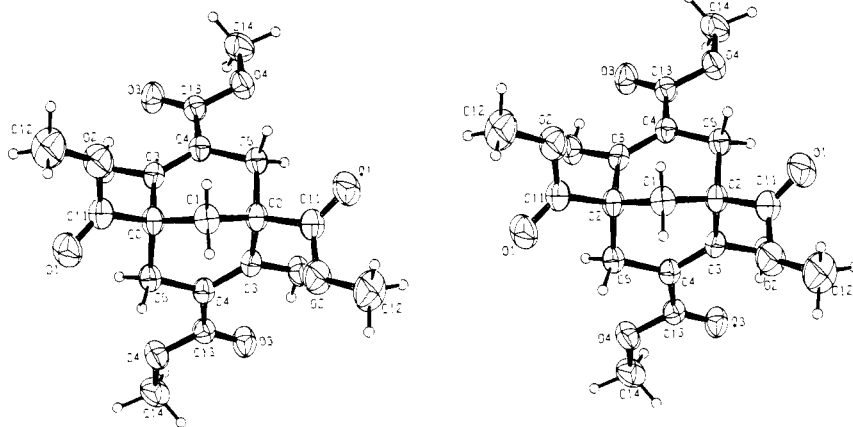
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Figure 1. Stereoview of the X-ray structure of 1. The view is along the crystallographic 2-fold axis through C(1). O(5) is partly hidden underneath O(2). The configuration of the isomer shown is $1R,5R$.[14]

Table I. Bond Lengths (Å) in 1 with Standard Deviations in Parentheses

| O(1)–C(11) | 1.192 (3) | C(1)–C(2) | 1.531 (3) |
| O(2)–C(11) | 1.328 (3) | C(2)–C(3) | 1.516 (3) |
| O(2)–C(12) | 1.443 (4) | C(2)–C(11) | 1.530 (3) |
| O(3)–C(13) | 1.226 (3) | C(2)–C(5)' | 1.534 (3) |
| O(4)–C(13) | 1.333 (3) | C(3)–C(4) | 1.353 (3) |
| O(4)–C(14) | 1.447 (3) | C(4)–C(5) | 1.511 (3) |
| O(5)–C(3) | 1.346 (3) | C(4)–C(13) | 1.452 (3) |

Table II. Bond Angles (deg) in 1 with Standard Deviations in Parentheses

| C(11)–O(2)–C(12) | 116.5 (2) | C(2)–C(3)–C(4) | 123.8 (2) |
| C(13)–O(4)–C(14) | 116.0 (2) | C(3)–C(4)–C(5) | 121.9 (2) |
| C(2)–C(1)–C(2)' | 107.9 (2) | C(3)–C(4)–C(13) | 118.4 (2) |
| C(1)–C(2)–C(3) | 110.3 (2) | C(5)–C(4)–C(13) | 119.6 (2) |
| C(1)–C(2)–C(11) | 109.2 (2) | C(4)–C(5)–C(2)' | 110.9 (2) |
| C(1)–C(2)–C(5)' | 108.8 (2) | O(1)–C(11)–O(2) | 123.7 (2) |
| C(3)–C(2)–C(11) | 109.4 (2) | O(1)–C(11)–C(2) | 125.1 (2) |
| C(3)–C(2)–C(5)' | 109.4 (2) | O(2)–C(11)–C(2) | 111.1 (2) |
| C(11)–C(2)–C(5)' | 109.7 (2) | O(3)–C(13)–O(4) | 121.4 (2) |
| O(5)–C(3)–C(2) | 111.9 (2) | O(3)–C(13)–C(4) | 124.6 (2) |
| O(5)–C(3)–C(4) | 124.3 (2) | O(4)–C(13)–C(4) | 113.9 (2) |

1 exists exclusively in the dienol form (1b) in solution. Stabilization by conjugate chelation, involving intramolecular hydrogen bonding of the type O—H···O=C between the hydroxyl group on C-2 (or C-6) and the ester carbonyl group on C-3 (or C-7) is abetted by relief of steric strain through the removal of the endo protons on C-3 and C-7 in the twin-chair conformation of 1a.[7]

**Infrared Spectra.** Stretching frequencies in the 1600–1700-cm⁻¹ region of the IR spectrum of 1 in CCl₄ provide independent evidence for the exclusive presence of 1b. Absorptions at 1620 and 1660 cm⁻¹, due to conjugated C=C and hydrogen-bonded C=O stretching modes, are comparable to the values of 1618 and 1656 cm⁻¹ reported for 2b.[9] An absorption at 1745 cm⁻¹, due to the ester C=O stretching mode of the carbonyl groups on C-1 and C-5, is comparable to the value of 1744 cm⁻¹ reported for the ester C=O stretch in 2a.[9] On the other hand, there is no absorption near 1718 cm⁻¹, the value reported for the ketonic carbonyl stretch in 2a.[9]
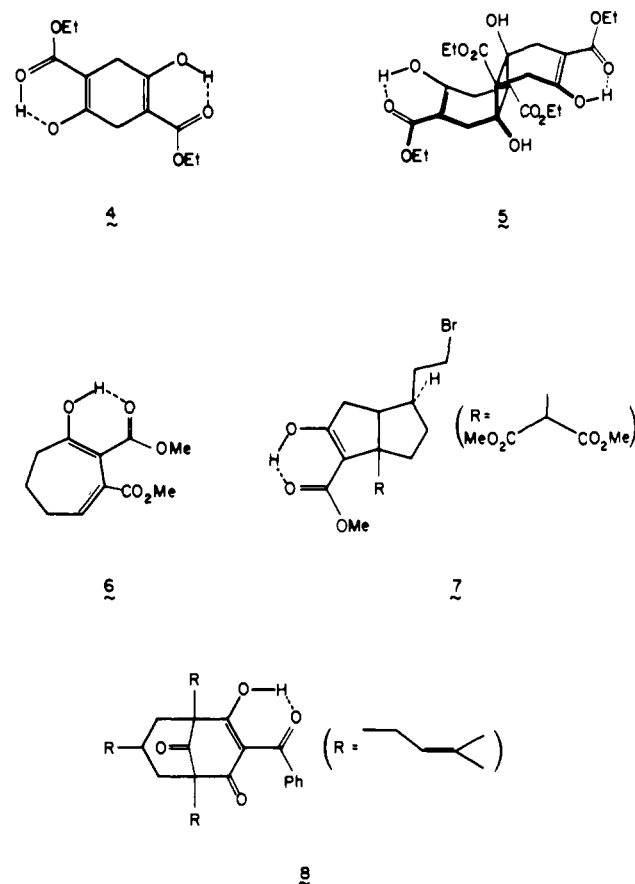
A broad, weak absorption between 2500 and 3500 cm⁻¹ in the IR spectrum of 1 is characteristic of an OH stretching mode where the hydroxyl group is involved in conjugate chelation. Similar bands have been observed, for example, in the spectra of conjugated enolized β-diketones.[10]

It remains to be noted that there is no absorption at or near 1490 cm⁻¹ in the IR spectrum of 1. The presence of this band in bicyclo[3.3.1]nonanes has been ascribed[8] to nonbonded interaction between the endo hydrogens on C-3 and C-7 in the twin-chair conformation, and its absence may therefore be taken to indicate the absence of such interactions, i.e., as evidence for the absence of the diketo tautomer 1a in CCl₄ solution.

(7) According to empirical force field calculations, bicyclo[3.3.1]nonane prefers the twin-chair conformation [Peters, J. A.; Baas, J. M. A.; van de Graaf, B.; van der Toorn, J. M.; van Bekkum, H. *Tetrahedron* **1978**, *34*, 3313 and references therein. Ōsawa, E.; Aigami, K.; Inamoto, Y. *J. Chem. Soc., Perkin Trans. 2* **1979**, 172 and references therein.] Infrared studies[8] lead to the same conclusion. See also ref 3.

(8) Eglinton, G.; Martin, J.; Parker, W. *J. Chem. Soc.* **1965**, 1243.

(9) Leonard, N. J.; Gutowsky, H. S.; Middleton, W. J.; Petersen, E. M. *J. Am. Chem. Soc.* **1952**, *74*, 4070.

(10) Rasmussen, R. S.; Tunnicliff, D. D.; Brattain, R. R. *J. Am. Chem. Soc.* **1949**, *71*, 1068. See also: Schuster, P.; Zundel, G.; Sandorfy, C. "The Hydrogen Bond. II. Structure and Spectroscopy"; North Holland: Amsterdam, 1976; pp 603–605. Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; Chapman and Hall: London, 1975; pp 118–120.

Chart 1



**Structure of Meerweins's Ester in the Solid State.** The spectroscopic studies described above provide compelling evidence that in solution, Meerwein's ester exists in the dienol form (1b) to the

Table III.   Selected Parameters for X-ray Structures of
Some Cyclic β-Diketo Enols[a]

| atoms | 1[b] | 4[c] | 5[c,d] | 6[c] | 7[e] | 8[c] |
|---|---|---|---|---|---|---|
| | | | Interatomic Distances[f] | | | |
| C(3)–O(5) | 1.346 | 1.338 | 1.343 | 1.339 | 1.349 | 1.303 |
| C(3)–C(4) | 1.353 | 1.352 | 1.349 | 1.362 | 1.341 | 1.388 |
| C(4)–C(13) | 1.452 | 1.455 | 1.445 | 1.436[g] | 1.451 | 1.447 |
| C(13)–O(3) | 1.226 | 1.216 | 1.223 | 1.217[h] | 1.223 | 1.266 |
| O(3)···O(5) | 2.573 | 2.615 | 2.614 | 2.576 | 2.658 | 2.418 |
| | | | Bond Angles[i] | | | |
| O(5)–C(3)–C(4) | 124.3 | 125.1 | 125.6 | 122.8 | 126.4 | 121.6 |
| C(3)–C(4)–C(13) | 118.4 | 118.9 | 119.3 | 118.4[j] | 120.6 | 118.1 |
| C(4)–C(13)–O(3) | 124.6 | 124.7 | 124.0 | 126.4[k] | 123.1 | 118.7 |

[a] Compound no. 4–8 correspond to structural formulas depicted
in Chart I.   [b] Crystals of Meerwein's ester from methanol.
Structural parameters were calculated by the interactive program
GEOM.   [c] Structural parameters were calculated by the Cambridge
crystallographic database program GEOM78.   [d] Values refer to the
conjugate chelate.   The other β-keto ester hydrogen bond in this
molecule is not part of an enolic system.   [e] Structural parameters
were calculated by the interactive program GEOM using atom
coordinates kindly provided by James P. Springer.   [f] In angstroms.
[g] Reported[15] 1.443 Å.   [h] Reported[15] 1.229 Å.   [i] In degrees.
[j] Reported[15] 119.2°.   [k] Reported[15] 124.9°.

virtual exclusion of the diketo tautomer (1a).[11]   Further spec-
troscopic evidence suggested that 1b is also the dominant and
possibly exclusive form in the solid state.   Thus, the positions and
intensities of the IR bands of 1 in solution (CCl₄) and in the solid
state (KBr) were found to be essentially identical, and a high
degree of similarity was observed in the ¹³C NMR spectra of
CDCl₃ solutions and of solid samples of 1 (Experimental Section).

However, this conclusion stood in direct contradiction to an
earlier conclusion by Meerwein and Schürmann,[2a] who had also
considered the question of tautomerism in 1.   On the basis of
various observations,[12] these workers had assigned the diketo
structure (1a) to 1 and to several of its derivatives[13] in the solid
state, including the 1,5-dicarboxylic acid (3).   We therefore turned
to single-crystal X-ray analysis for a definitive answer to this
question.

Crystals of 1 from methanol are orthorhombic, space group
*Pbcn*, with four molecules in a unit cell.   The molecule is located
on a crystallographic 2-fold axis that passes through C-9.   A stereo
view of the X-ray structure is shown in Figure 1, and selected bond
lengths and bond angles are given in Tables I and II.[14]   The point
at issue being the tautomeric identity of 1, we focus attention on
the structural parameters that are associated with the enolic β-keto
ester fragment O(3)=C(13)–C(4)=C(3)–O(5)–H.   Values for
these are listed in Table III, along with corresponding values for
structurally related enols 4–8 (Chart I)[15] reported in the crys-

(11) Similarly, spectroscopic evidence has indicated that 2,4,6,8-tetra-
carbomethoxybicyclo[3.3.0]octane-3,7-dione and 2,4,6,8-tetracarbomethoxy-
bicyclo[3.3.1]nonane-3,7-dione exist predominantly in the dienol form.   See:
Yates, P.; Hand, E. S.; French, G. B. *J. Am. Chem. Soc.* **1960**, *82*, 6347.
Bertz, S. H.; Adams, W. O.; Silverton, J. V. *J. Org. Chem.* **1981**, *46*, 2828.
(12) For example, Meerwein and Schürmann argued[2a] that the slow de-
velopment of the reddish violet coloration typical of enols seen upon addition
of ferric chloride to freshly prepared *cold* solutions of 1 indicated progressive
enolization of the initially present diketo form 1a.
(13) Along with 1, diketo structures were assigned[2a] to 1,5-dicarboxy-
3,7-dicarbomethoxybicyclo[3.3.1]nonane-2,6-dione (3) and to 3,7-dicarbo-
methoxybicyclo[3.3.1]nonane-2,6-dione, products of partial hydrolysis and
hydrolysis–decarboxylation of 1, respectively.   However, the spectral char-
acteristics of 3 (Experimental Section), like those of 1, plainly indicate that
this compound is also in the dienol form.
(14) The following correspondence obtains between carbon atom names
in the crystal structure [C(n)] and carbon atom numbers in the bicyclo-
[3.3.1]nonane skeleton (C-n): C(1) ~ C-9, C(2) ~ C-1 or C-5, C(3) ~ C-2
or C-6, C(4) ~ C-3 or C-7, C(5) ~ C-4 or C-8.
(15) 3: Mez, H.-C.; Rihs, G. *Helv. Chim. Acta* **1973**, *56*, 2766.   4: Mez,
H.-C.; Rihs, G. *Helv. Chim. Acta* **1973**, *56*, 2772.   5: Hunter, W. E; Atwood,
J. L.; Lampert, B. A.; Garner, R. H. *J. Cryst. Mol. Struct.* **1976**, *6*, 291.   6:
Danishefsky, S.; Vaughn, K.; Gadwood, R. C.; Tsuzuki, K.; Springer, J. P.
*Tetrahedron Lett.* **1980**, *21*, 2625.   7: McCandlish, L. E.; Hanson, J. H.;
Stout, G. H.; *Acta Crystallogr., Sect. B* **1976**, *B32*, 1793.

Table IV.   Bond Lengths (Å) in 1·4B with Standard
Deviations in Parentheses

| | | | |
|---|---|---|---|
| O(1)–C(11) | 1.162 (10) | C(4)–C(13) | 1.462 (10) |
| O(2)–C(11) | 1.346 (11) | C(21)–C(22) | 1.349 (20) |
| O(2)–C(12) | 1.463 (9) | C(21)–C(26) | 1.366 (21) |
| O(3)–C(13) | 1.213 (10) | C(22)–C(23) | 1.349 (22) |
| O(4)–C(13) | 1.316 (10) | C(23)–C(24) | 1.357 (23) |
| O(4)–C(14) | 1.442 (10) | C(24)–C(25) | 1.314 (23) |
| O(5)–C(3) | 1.351 (9) | C(25)–C(26) | 1.334 (22) |
| C(1)–C(2) | 1.589 (9) | C(31)–C(32) | 1.332 (28) |
| C(1)–C(2)' | 1.589 (9) | C(31)–C(33)' | 1.366 (26) |
| C(2)–C(3) | 1.502 (10) | C(32)–C(33) | 1.349 (26) |
| C(2)–C(11) | 1.545 (10) | C(41)–C(42) | 1.339 (22) |
| C(2)–C(5)' | 1.506 (10) | C(41)–C(43) | 1.375 (25) |
| C(3)–C(4) | 1.346 (11) | C(42)–C(43)' | 1.349 (21) |
| C(4)–C(5) | 1.498 (10) | | |

Table V.   Bond Angles (deg) in 1·4B with Standard Deviations
in Parentheses

| | | | |
|---|---|---|---|
| C(11)–O(2)–C(12) | 115.2 (6) | O(1)–C(11)–C(2) | 125.2 (8) |
| C(13)–O(4)–C(14) | 116.8 (6) | O(2)–C(11)–C(2) | 110.4 (6) |
| C(2)–C(1)–C(2)' | 106.4 (8) | O(3)–C(13)–O(4) | 122.9 (7) |
| C(1)–C(2)–C(3) | 107.1 (5) | O(3)–C(13)–C(4) | 125.6 (8) |
| C(1)–C(2)–C(11) | 109.2 (6) | O(4)–C(13)–C(4) | 111.5 (7) |
| C(1)–C(2)–C(5)' | 106.7 (5) | C(22)–C(21)–C(26) | 119.2 (12) |
| C(3)–C(2)–C(11) | 109.5 (6) | C(21)–C(22)–C(23) | 120.2 (12) |
| C(3)–C(2)–C(5)' | 114.7 (6) | C(22)–C(23)–C(24) | 119.9 (13) |
| C(11)–C(2)–C(5)' | 109.7 (6) | C(23)–C(24)–C(25) | 119.1 (13) |
| O(5)–C(3)–C(2) | 107.9 (6) | C(24)–C(25)–C(26) | 122.5 (13) |
| O(5)–C(3)–C(4) | 124.5 (6) | C(21)–C(26)–C(25) | 119.0 (13) |
| C(2)–C(3)–C(4) | 126.7 (7) | C(32)–C(31)–C(33)' | 120.9 (15) |
| C(3)–C(4)–C(5) | 121.1 (6) | C(31)–C(32)–C(33) | 119.7 (13) |
| C(3)–C(4)–C(13) | 117.9 (7) | C(32)–C(33)–C(31)' | 119.3 (15) |
| C(5)–C(4)–C(13) | 120.9 (7) | C(42)–C(41)–C(43) | 118.8 (13) |
| C(4)–C(5)–C(2)' | 110.4 (6) | C(41)–C(42)–C(43)' | 120.7 (13) |
| O(1)–C(11)–O(2) | 124.4 (7) | C(41)–C(43)–C(42)' | 120.5 (12) |

tallographic literature.[16]   Inspection of Table III reveals that
interatomic distances and bond angles in 1 are comparable to those
in other enolized compounds.   Note in particular that the C-
(3)–C(4) bond lengths are compatible only with slightly stretched
C–C double bonds.   These findings leave no doubt that 1 is in the
dienol form in the solid state, as well as in solution.

**Benzene Solvate of Meerwein's Ester.**   As originally reported
by Meerwein and Schürmann,[2a] crystals of 1 from benzene contain
solvent of crystallization.   To complete our study of Meerwein's
ester, the crystal structure of this solvate was determined.   The
benzene is very loosely held (partial desolvation occurs just on
standing in air at room temperature) and special precautions were
therefore necessary to prevent loss of benzene from the crystal
during data collection (see Experimental Section).

The crystals are orthorhombic, space group *Pnaa*, with four
stoichiometric benzene molecules per molecule of ester (1·4B).[17]
In the crystal, the ester molecules and half of the benzene mol-
ecules are found in special positions.   The ester molecules are
located on crystallographic 2-fold rotation axes.   Of the four
stoichiometric benzene molecules, two are in general positions
[ring-2 = C(21), ..., C(26); one independent molecule per half-ester
and per unit cell] and the other two are located on crystallographic
centers of symmetry [two independent half-rings, ring-3 C(31),
C(32), C(33) and ring-4 C(41), C(42), C(43)].   Selected bond
lengths and bond angles are given in Tables IV and V.   Com-
parison of corresponding values in Tables I and IV and in Tables
II and V shows that there are no major differences in the structures
of the solvated and unsolvated ester molecule.   In particular, bond
lengths in the enolized β-keto ester fragment of the solvate differ
by no more than 0.01 Å from the values reported for 1 in Table

(16) These structures were selected as most appropriate for the purpose
of comparison with 1 among those reported in the Cambridge crystallographic
database, updated to Jan 1982.
(17) This stoichiometry was independently determined from relative inte-
grated intensities in the ¹H NMR spectrum of freshly crystallized benzene
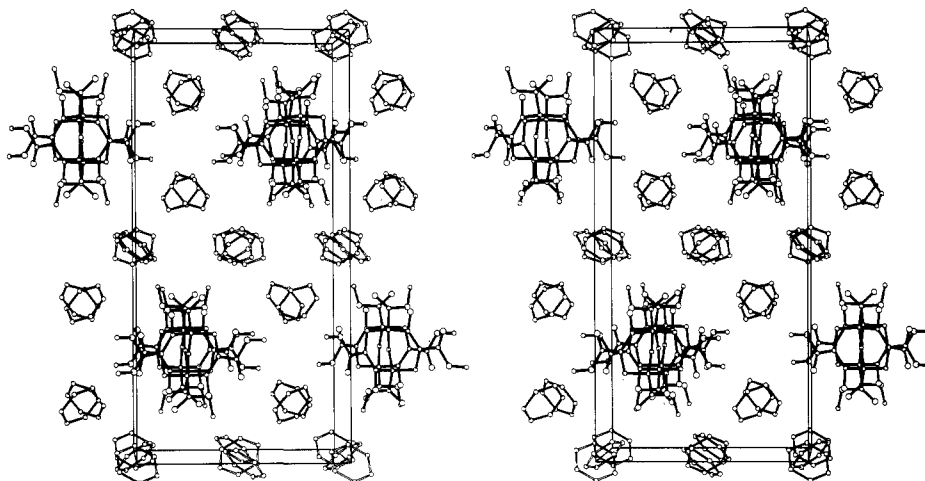solvate (Experimental Section).

**Figure 2.** Molecular packing in the crystal of 1·4B. The view is down the *a* axis with the *b* axis horizontal and the *c* axis vertical. Four columns of ester molecules are shown, of which two columns pass through the unit cell shown in the figure and the other two columns pass through adjacent cells. Each column of ester molecules is encased within a cylinder comprised of eight parallel columns of benzene molecules. The set of benzene molecules that occupy general positions in the unit cell are shown with solid bonds and the two sets of benzene molecules that are located on inversion centers are shown with open bonds. The sets of benzene molecules located in the inversion centers form infinite planes of benzene molecules normal to the *c* axis and spaced *c*/2 apart. Hydrogen atoms and bonds to hydrogen atoms are not shown.
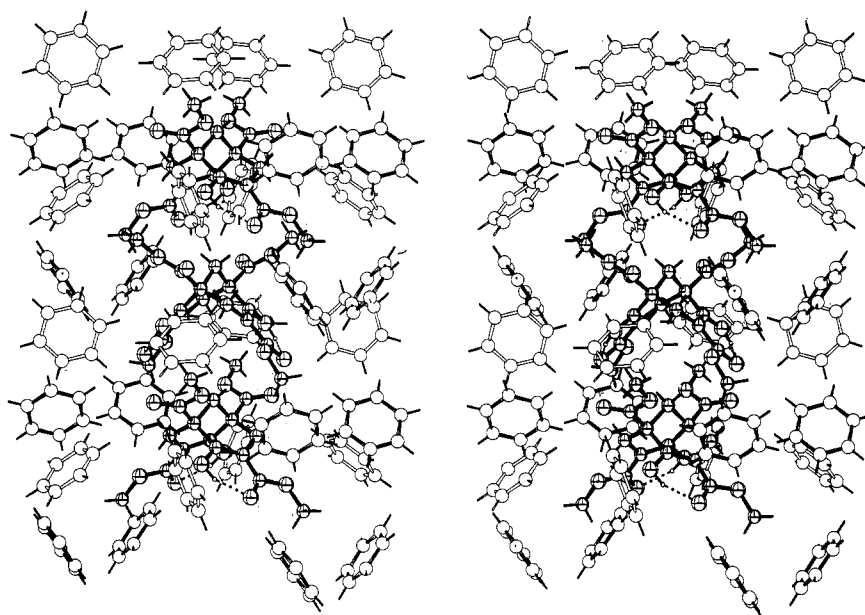


**Figure 3.** This figure illustrates the solvation of the ester molecules along a segment of the ester column. The view is normal to the column. The intramolecular hydrogen bonds in the esters are dashed. The bonds in the benzene molecules are shaded as in Figure 2. The sense of chirality of the ester molecules alternates from molecule to molecule along the column.

III, and corresponding bond angles also differ by no more than 1°. The O(3)···O(5) distance in 1·4B is 2.591 Å.

As suggested by the stoichiometry of the complex, in which benzene contributes almost half of the heavy atoms and constitutes almost half of the molecular weight, and as fully borne out by examination of the crystal structure, it is not clear whether the ester is the host or the guest molecule. In the unit cell (Figure 2), molecules of 1 are seen to be partly surrounded by benzene molecules and vice versa. A typical ester molecule is surrounded by two neighboring ester molecules with the opposite sense of chirality and by sixteen benzene molecules. The two neighboring ester molecules are found above and below the ester by translation along the 2-fold rotation axis. The sixteen benzene rings, comprising eight ring-2, four ring-3, and four ring-4 molecules, are found in two bands about the girth of the ester molecule. This sheathing of 1 in a channel of benzene molecules is clearly seen in Figure 3.

Computer modeling of space-filling structures indicates snug packing of the molecules in the crystal of 1·4B. Although the crystallographic $C_2$ symmetry of 1 might be expected to facilitate

formation of inclusion compounds,[18] preliminary experiments have given no indication that this is the general case.[19] However, it should also be noted that the ambiguity in the host–guest relationship exhibited for 1·4B seems to have few precedents among crystalline inclusion compounds.[20,21]

(18) Bishop, R.; Dance, I. *J. Chem. Soc., Chem. Commun.* **1979**, 992. Chan, T.-L.; Mak, T. C. W.; Trotter, J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 672. Huang, N. Z.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1982**, 543.

(19) No solvent is included in 1 crystallized from toluene, 1,3,5-trimethylbenzene, pyridine, cyclohexane, or methanol.

(20) For reviews, see: Cramer, F. "Einschlussverbindungen"; Springer: Heidelberg, 1954. Cramer, F. *Rev. Pure Appl. Chem.* **1955**, *5*, 143. Mandelcorn, L. *Chem. Rev.* **1959**, *59*, 827. Asselineau, C.; Asselineau, J. *Ann. Chim.* **1964**, *9*, 461. Frank, S. G. *J. Pharm. Sci.* **1975**, *64*, 1585. MacNicol, D. D.; McKendrick, J. J.; Wilson, D. R. *Chem. Soc. Rev.* **1978**, *7*, 65. Davies, J. E. D. *J. Mol. Struct.* **1981**, *75*, 1.

(21) A rare example of this type of dodecaphenylcyclohexagermane, which forms an inclusion compound containing seven molecules of benzene per molecule of Ge₆Ph₁₂. See: Dräger, M.; Ross, L.; Simon, D. *Z. Anorg. Allg. Chem.* **1980**, *466*, 145.

## Experimental Section

NMR spectra were recorded on a Bruker WM-250 spectrometer operated at 250.132 MHz for proton spectra and 62.896 MHz for carbon spectra. Residual solvent resonances were used as internal reference. CP-MAS carbon spectra of solid samples were recorded on an IBM NR-80 spectrometer operated at 20.13 MHz and were externally referenced. Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrometer using 0.5 mm pathlength cells to contain $CCl_4$ solutions of 1; solid state IR spectra were obtained from KBr pellets. Melting points were measured in a Thomas-Hoover capillary melting point apparatus and are corrected.

**1,3,5,7-Tetracarbomethoxybicyclo[3.3.1]nona-2,6-diene-2,6-diol, Meerwein's ester (1),** was prepared by the method of Schaefer and Honig[2b,22] and twice recrystallized from benzene after hot filtration. The melting behavior of freshly crystallized 1 varied substantially with the rate of heating. Gradual heating from room temperature caused sintering to occur at ca. 55 °C and then melting between 145 and 155 °C. Immersion of the sample into a bath preheated above 60 °C caused instant melting. The melting point after thorough drying (several days in the open air or vacuum drying overnight) was 164–166 °C. Further purification of the powdery white solid thereby obtained by recrystallization from methanol produced colorless prisms with mp 166.5–167.5 °C (lit.[2a] mp 163–164 °C). (These colorless prisms are quite different in habit from those obtained by crystallization from benzene, which form long prismatic needles with fine striations parallel to the needle and crystallographic *a* axis). $^1$H NMR ($CDCl_3$) δ 2.30 (s, 2 H, H-9), 2.85 (s, 4 H, H-4, H-4' and H-8, H-8'), 3.74 (s, 6 H, OMe), 3.75 (s, 6 H, OMe), 7.27 (s, 24 H, benzene),[23] 12.14 (s, 2 H, OH, exchanges with $D_2O$, shift independent of concentration). The $^1$H NMR spectrum in benzene-$d_6$ resolves some accidental isochronies that occur in other solvents: $^1$H NMR (benzene-$d_6$) δ 2.43 (s, 2 H, H-9), 3.18 (d, 2 H, H-4, H-8, $^2J_{HH}$ = 16.5 Hz), 3.18 (s, 6 H, OMe), 3.36 (d, 2 H, H-4', H-8', $^2J_{HH}$ = 16.5 Hz), 3.53 (s, 6 H, OMe), 12.97 (s, 2 H, OH); $^{13}C\{^1H\}$ NMR ($CDCl_3$)[24] δ 29.74 (C-4, C-8), 35.35 (C-9), 47.72 (C-1, C-5), 51.82 (OMe), 52.63 (OMe), 96.85 (C-3, C-7), 168.18 (C-2, C-6), 171.81 (CO), 172.40 (CO); CP-MAS $^{13}$C NMR (neat solid crystallized from benzene, with included solvent removed) δ 47.7 (C-1, C-5), 50.4 (OMe), 52.8 (OMe), 95.6 (C-3, C-7), 168.5 (C-2, C-6), 171.8 (2 CO); IR[9,27] (75 mg/mL $CCl_4$; saturated solution) 1200–1270 (asymmetric carboxylate CO stretch), 1335 (symmetric $CH_3$ bend), 1360 (symmetric $CH_3$ bend), 1440 (asymmetric $CH_3$ bend), 1620 (conjugated olefin stretch), 1660 (H-bonded 3,7-carboxylate CO stretch), 1745 (1,5-carboxylate CO stretch), 2955 (CH stretch), 3000 cm$^{-1}$ (br w chelated OH); IR (KBr) 1190–1290 (asymmetric carboxylate CO stretch), 1325 (symmetric $CH_3$ bend), 1360 (symmetric $CH_3$ bend), 1440 (asymmetric $CH_3$ bend), 1620 (conjugated olefin stretch), 1660 (H-bonded, 3,7-carboxylate CO stretch), 1740 (1,5-carboxylate CO stretch), 2950 (CH stretch), 3000 cm$^{-1}$ (br w chelated OH).

**1,5-Dicarboxy-3,7-dicarbomethoxybicyclo[3.3.1]nona-2,6-diene-2,6-diol** (3) was prepared by the method of Meerwein and Schürmann.[2a,28] The pinkish solid was recrystallized from methanol-water to yield a pink-tinged, crystalline product with a decomposition point at 229 °C ($CO_2$ evolution): $^1$H NMR (2:1 $CDCl_3$-acetone-$d_6$) δ 2.36 (s, 2 H, H-9), 2.80 (AB dd, 4 H, H-4, H-8 and H-4', H-8', $^2J_{HH}$ = 16.8 Hz, δν = 9.5 Hz), 3.73 (s, 6 H, OMe), 12.20 (br s, 2 H, enolic OH). No resonance was observed for the carboxylic acid protons. The resonances for the exo and endo protons on C-4 and C-8 are well resolved in $Me_2SO$-$d_6$ and occur as an AB doublet of doublets at 2.61 and 2.74 ppm ($^2J_{HH}$ = 16.6 Hz);

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(22) A solid mass that formed upon addition of NaOMe to the initially formed condensate was broken up before refluxing.

(23) Observed for a sample of 1 freshly crystallized from benzene.

(24) Of particular note are the assignments of the C-2 (C-6) and C-3 (C-7) resonances. The enol carbon C-2 (C-6) resonance of 168.18 ppm is similar to that determined by SCS (substituent chemical shift) methods[25] for the methoxy-substituted carbon of MeO—(—C—C—)C═C(—C—C—)—COOMe, 167 ppm. The C-3 (C-7) resonance at 96.85 ppm is due to a quaternary carbon, the shift of which corresponds to that calculated for the ester-substituted olefinic carbon by SCS methods (98 ppm). The remainder of the resonances were assigned by J-resolved[26] and off-resonance $^{13}$C spectroscopy.

(25) Wehrli, F. W.; Wirthlin, T. "Interpretation of $^{13}$C NMR Spectra"; Heyden: London, 1978; p 41.

(26) Several types of $^{13}$C spin-echo J-modulation experiments have been reported. See: Jakobsen, H. J.; Sørensen, O. W.; Brey, W. S.; Kanyha, P. *J. Magn. Reson.* **1982,** *48,* 328. Pei, F. K.; Freeman, R. *J. Magn. Reson.* **1982,** *48,* 318. A simple version of this technique was used, as supplied by Bruker.

(27) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 3d ed.; Wiley: New York, 1974; pp 86, 103, 104, 140.

(28) With the modification that freshly purchased barium hydroxide was used in place of recrystallized material.

Table VI.   Final Atomic Parameters for $1^{a,b}$

| atom | x | y | z |
|------|------|------|------|
| O(1) | 0.3223 (2) | 0.22734 (13) | 0.05982 (11) |
| O(2) | 0.1768 (2) | 0.20923 (14) | 0.17614 (11) |
| O(3) | 0.1282 (2) | 0.52470 (11) | 0.31133 (9) |
| O(4) | 0.2621 (2) | 0.49748 (11) | 0.43065 (8) |
| O(5) | 0.2029 (2) | 0.42355 (11) | 0.18187 (9) |
| C(1) | 0.5000 | 0.24083 (21) | 0.25000 |
| C(2) | 0.4118 (3) | 0.30581 (14) | 0.18722 (12) |
| C(3) | 0.3110 (3) | 0.38061 (14) | 0.23295 (13) |
| C(4) | 0.3324 (3) | 0.40394 (15) | 0.31447 (13) |
| C(5) | 0.4617 (3) | 0.35674 (14) | 0.36769 (13) |
| C(11) | 0.3007 (3) | 0.24400 (15) | 0.13226 (15) |
| C(12) | 0.0596 (4) | 0.15236 (23) | 0.13063 (21) |
| C(13) | 0.2313 (3) | 0.47927 (15) | 0.35019 (13) |
| C(14) | 0.1709 (3) | 0.57571 (19) | 0.46783 (16) |

$^a$ Standard deviations are in parentheses.   $^b$ Anisotropic thermal parameters and final atomic parameters for hydrogen atoms are recorded in the supplementary material.

Table VII.   Final Atomic Parameters for $1·4B^{a,b}$

| atom | x | y | z |
|------|------|------|------|
| O(1) | 0.7423 (5) | 0.8158 (4) | 0.6197 (2) |
| O(2) | 0.7754 (5) | 0.6529 (4) | 0.6477 (2) |
| O(3) | 0.4011 (4) | 0.5194 (4) | 0.7021 (2) |
| O(4) | 0.4378 (4) | 0.4871 (4) | 0.7857 (2) |
| O(5) | 0.5204 (4) | 0.6645 (4) | 0.6570 (2) |
| C(1) | 0.7372 (9) | 0.7500 | 0.7500 |
| C(2) | 0.6569 (6) | 0.7600 (6) | 0.7005 (3) |
| C(3) | 0.5741 (6) | 0.6705 (5) | 0.7034 (3) |
| C(4) | 0.5440 (6) | 0.6165 (6) | 0.7465 (3) |
| C(5) | 0.6049 (6) | 0.6317 (5) | 0.7972 (3) |
| C(11) | 0.7282 (6) | 0.7493 (7) | 0.6503 (3) |
| C(12) | 0.8412 (7) | 0.6321 (8) | 0.6005 (3) |
| C(13) | 0.4551 (7) | 0.5372 (6) | 0.7414 (3) |
| C(14) | 0.3448 (8) | 0.4139 (7) | 0.7871 (3) |
| C(21) | 0.2320 (13) | 0.1764 (8) | 0.8569 (6) |
| C(22) | 0.2610 (9) | 0.2383 (13) | 0.8976 (5) |
| C(23) | 0.1993 (15) | 0.3247 (12) | 0.9092 (4) |
| C(24) | 0.1076 (13) | 0.3492 (9) | 0.8799 (7) |
| C(25) | 0.0814 (10) | 0.2889 (13) | 0.8399 (6) |
| C(26) | 0.1416 (14) | 0.2039 (12) | 0.8269 (5) |
| C(31) | 1.0629 (11) | 0.5821 (15) | 0.5154 (7) |
| C(32) | 1.0716 (11) | 0.4908 (19) | 0.5410 (4) |
| C(33) | 1.0080 (17) | 0.4077 (11) | 0.5263 (8) |
| C(41) | 0.4234 (14) | 0.5440 (14) | 0.5334 (4) |
| C(42) | 0.3959 (10) | 0.4581 (13) | 0.5057 (6) |
| C(43) | 0.5294 (17) | 0.5863 (8) | 0.5274 (5) |

$^a$ Standard deviations are in parentheses.   $^b$ Anisotropic thermal parameters and final atomic parameters for hydrogen atoms are recorded in the supplementary material.

$^{13}C\{^1H\}$ NMR (acetone-$d_6$) δ 36.50 (C-9), 48.35 (C-1, C-5), 52.41 (OMe), 97.61 (C-3, C-7), 169.82 (C-2, C-6), 172.60 (CO), 173.40 (CO). The signal due to C-4, C-8 was obscured by the acetone multiplet centered at 29.8 ppm. IR[9,27] (KBr) 1210 (asymmetric CO stretch), 1270 (asymmetric CO stretch), 1345 (symmetric $CH_3$ bend), 1365 (symmetric $CH_3$ bend), 1440 (asymmetric $CH_3$ bend), 1615 (conjugated olefin stretch), 1655 (H-bonded carboxylate CO stretch), 1725 (carboxylic acid CO stretch), 2950 (CH stretch), 2300 to 3700 cm$^{-1}$ (carboxylic acid OH stretch).

**Crystallography.** Crystals of 1 from methanol were orthorhombic, space group *Pbcn*, with *a* = 8.235 (1) Å, *b* = 13.870 (2) Å, *c* = 15.963 (3) Å, and $d_{calcd}$ = 1.400 g cm$^{-3}$ for Z = 4 ($C_{17}H_{20}O_{10}$, $M_r$ 384.34). Crystals of 1·4B were orthorhombic, space group *Pnaa*, with *a* = 11.867 (2) Å, *b* = 12.667 (1) Å, *c* = 25.601 (3) Å, and $d_{calcd}$ = 1.203 g cm$^{-3}$ for Z = 4 ($C_{17}H_{20}O_{10}·4C_6H_6$, $M_r$ 696.79). The intensity data were measured at room temperature on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pluse-height discrimination). The size of the crystal used for data collection was approximately 0.35 × 0.50 × 0.65 mm for 1 and 0.12 × 0.20 × 0.45 mm for 1·4B. A total of 1229 (1) and 2601 (1·4B) independent reflections were measured for θ < 57°, of which 1173 (1) and 1363 (1·4B) were considered to be observed [$I$ < 2.5σ($I$)]. The structure was solved by a multiple-solution procedure[29] and was

(29) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971,** *A27,* 368.

refined by full-matrix least squares.

Special precautions were required to prevent loss of benzene from crystals of 1·4B during data collection. The crystal was mounted by placing it inside a 0.5-mm Lindemann glass capillary, then drawing some benzene into the tube by capillary action, and finally sealing the two ends of the tube with epoxy cement. The crystal orientation shifted only once, prior to data collection, and remained stable during the data collection period. There was no apparent deterioration of the crystal during this period; although there was occasional ±5% variation in the intensity of individual reference reflections, the average of the five reference reflections remained constant within ±1%.

Sixteen reflections in 1 that were strongly affected by extinction were excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indexes for 1 are $R = 0.051$ and $wR = 0.068$ for the remaining 1157 observed reflections; the final difference map has no peaks greater than

±0.2 e Å$^{-3}$. For 1·4B, the final discrepancy indexes are $R = 0.086$ and $wR = 0.076$ for the 1363 observed reflections. The final difference map has no peaks greater than ±0.3 e Å$^{-3}$ except for two peaks of 0.5 e Å$^{-3}$. Final atomic parameters for 1 and 1·4B are given in Tables VI and VII, respectively (see paragraph at end of paper regarding supplementary material).

**Supplementary Material Available:** Final anisotropic thermal parameters and atomic parameters for hydrogen atoms in 1 and 1·4B, distances less than 4 Å between the nonhydrogen atoms of the ester and carbon atoms of the neighboring benzene molecules in 1·4B (Tables VIII–XII) (5 pages). Ordering information is given on any current masthead page.

# 13C–1H Coupling Constants in Carbocations. 4.[1] Conformations of Internal Cyclopropylcarbinyl Cations (Benzobicyclo[4.1.0]heptyl Cations) and Their Rearrangements to Naphthalenium Cations

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**Abstract:** Ionizations of 2-substituted 1,1-dimethyl-3,4-methano-1,2,3,4-tetrahydronaphthalen-2-ols (**8**) (3,3-dimethylbenzobicyclo[4.1.0]heptan-2-ols) in FSO$_3$H/SO$_2$ClF at −130 °C do not yield the corresponding 2-cations but benzylic (4-) cations **10** as a result of cyclopropylcarbinyl–cyclopropylcarbinyl rearrangements. At higher temperatures, **10a** and **10b** undergo a further series of rearrangements to yield ultimately dialkylnaphthalenium cations. Comparison of the $^1J_{C_\alpha H}$ values of the internal cyclopropylcarbinyl cations with those of model bicyclic ketones give $\Delta J$ values of approximately 20 Hz, indicating that in all cases bisected cyclopropylcarbinyl geometries prevail. Conformations of these and related cations and of the bicyclic ketones are discussed.

Recently it has been reported that when 1,6-methano[10]-annulene is treated with FSO$_3$H/SO$_2$ClF at −100 °C, a monoprotonated cation is formed, which rearranges at −60 °C to a cyclopropylcarbinyl cation (**1**).[2] Observation of vicinal coupling
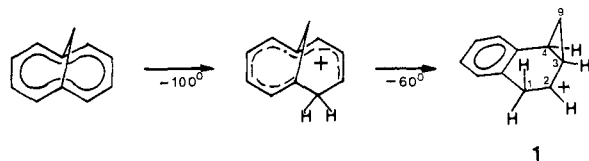


between H$_2$ and H$_3$ (7 Hz) but not between either of the protons at C$_1$ and H$_2$ led the authors to suggest that the structure of **1** may be "a more or less flat 'naphthalenium' skeleton" in which the cyclopropylcarbinyl moiety was not in the favored bisected arrangement, but one intermediate between that and the parallel conformation.[2] Support for such a structure was elicited from the calculations of Hehre and co-workers who showed the presence of two energy minima on either side of and 0.5 kcal higher than the most stable bisected conformation on the potential energy surface of the C$_4$H$_7^+$ species.[3]

We have developed a method for determining the conformations of carbocations, based on the difference, $\Delta J$, between the $^1J_{CH}$ value of the carbon adjacent to the cationic carbon in static classical cations and that in an appropriate model compound (ketone) according to eq 1, where $A$ is the maximum inductive

$$\Delta J = A - B \cos^2 \theta \qquad (1)$$

enhancement of $J_{C_\alpha H}$ (22.5 Hz for trialkyl cations) and $B$ is the maximum hyperconjugative diminution of $J_{C_\alpha H}$ (33.1 Hz for trialkylcations).[4] In the case of bisected cyclopropylcarbinyl cations **2–4**, the C$_\alpha$–H bond is orthogonal to the vacant p orbital



| | **2** | **3** | **4** |
|---|---|---|---|
| | $\Delta J$ | $\Delta J$ | $\Delta J$ |
| a, R = H | 27 | 22 | 22 |
| b, R = CH$_3$ | 24 | 20 | 21 |
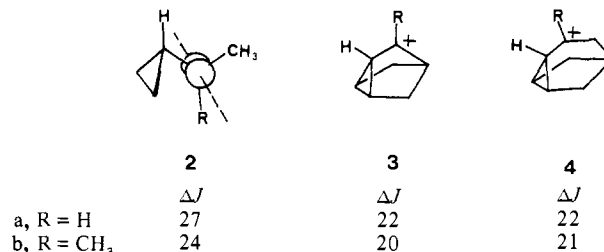
(1) Part 3: Kelly, D. P.; Farquharson, G. J.; Giansiracusa, J. J.; Jensen, W. A.; Hügel, H. M.; Porter, A. P.; Rainbow, I. J.; Timewell, P. H. *J. Am. Chem. Soc.* **1981**, *103*, 3539–3543.

(2) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 4528–4529.

(3) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5537–5539.

(4) Kelly, D. P.; Underwood, G. R.; Barron, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 3106–3111. Kelly, D. P.; Brown, H. C. *Ibid.* **1975**, *97*, 3897–3900.