

Crystal and Molecular Structure of Bis(9-triptycyl) Ketone and Bis(9-triptycyl)methane

Constance A. Johnson,^{1a} Alberto Guenzi,^{1a} Robert B. Nachbar, Jr.,^{1a} John F. Blount,^{1b} Olof Wennerström,^{1a,c} and Kurt Mislow^{*1a}

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544, and the Chemical Research Department, Hoffmann-La Roche, Inc., Nutley, New Jersey 07110. Received February 19, 1982

Abstract: The crystal and molecular structures of the title compounds, Tp_2CO and Tp_2CH_2 (Tp = 9-triptycyl), have been determined: for Tp_2CO , space group $A2/a$ (No. 15), $a = 16.760$ (3), $b = 19.885$ (3), $c = 28.738$ (5) Å, $\beta = 111.56$ (1)°, $Z = 12$, and for Tp_2CH_2 , space group $P2_1/c$ (No. 14), $a = 19.717$ (7), $b = 20.001$ (5), $c = 16.590$ (6) Å, $\beta = 112.23$ (2)°, $Z = 8$. There are two independent molecules in the unit cell of each compound. In Tp_2CO , one set of eight molecules occupies eight general positions (C_1 - Tp_2CO), while the remaining four are located on twofold rotation axes which pass through the carbonyl carbon and oxygen atoms (C_2 - Tp_2CO). In Tp_2CH_2 , both molecules (C_1 - and C_1' - Tp_2CH_2) occupy general positions; their conformations closely resemble those of C_1 - Tp_2CO and of the previously described Tp_2CHOH . The molecules are tightly meshed static gear systems. The values of the C-CO-C bond angles (128.5 and 128.8°) and of the C-CO bond lengths (1.531-1.566 Å) in C_1 - and C_2 - Tp_2CO , and of the C-CH₂-C bond angle (129.3°) and C-CH₂ bond lengths (1.532, 1.578 Å) in C_1 - Tp_2CH_2 , indicate that these systems are under considerable internal strain. Structural parameters for Tp_2CO and Tp_2CH_2 calculated by the empirical force-field (EFF) method are in satisfactory agreement with values determined by X-ray analysis. These calculations also reveal that the C_2 transition states for dynamic gearing lie 1.9 and 0.2 kcal mol⁻¹ above the C_2 ground states of Tp_2CO and Tp_2CH_2 , respectively; accordingly, C_2 - Tp_2CO corresponds to the ground state, and C_1 - Tp_2CO and Tp_2CH_2 , which have approximate C_2 symmetry, closely resemble gearing transition states. A set of two independent torsional coordinates, one for each Tp rotor, is derived from the calculated and experimentally derived torsion angles for Tp_2CH_2 , Tp_2CHOH , and Tp_2CO . It is shown that the structural correlation between these two independent parameters maps a minimum-energy region in the torsional space which corresponds to the calculated (EFF) dynamic gearing trajectory for Tp_2CH_2 .

As part of our continuing investigation of correlated rotation in sterically crowded molecules containing tightly coupled rotors,² we recently initiated a detailed study of correlated rotation in derivatives of bis(9-triptycyl)methane (Tp_2CH_2) and bis(9-triptycyl)carbinol (Tp_2CHOH).^{3,4} According to empirical force-field (EFF) calculations,³ the 9-triptycyl (Tp) moieties in these compounds undergo virtually unhindered correlated disrotation (dynamic gearing) by way of essentially isoenergetic C_2 and C_2' structures but exhibit high barriers to gear slippage. That is, the Tp rotors in Tp_2X behave as highly mobile yet tightly meshed gears. Experimental studies^{3,4} are fully in accord with this view.

Repulsive nonbonded interactions between the Tp groups in Tp_2CHOH result in an extraordinary widening of the central C-C-C bond angle, to 129°. The original impetus for the present work was an attempt to observe the effect on molecular geometry of two Tp groups attached to a carbonyl frame: significant deviations from the Tp_2CHOH structure might be anticipated in bis(9-triptycyl) ketone (Tp_2CO), given the shorter natural central C-CO bond distances, the wider natural central C-CO-C bond angle, and the lower coordination number of the central carbonyl carbon atom. For purposes of comparison with the X-ray structures of Tp_2CHOH and Tp_2CO , and with the structures calculated by the EFF method, the X-ray structure of Tp_2CH_2 was also determined in this work.

Results and Discussion

The ketone, Tp_2CO , was synthesized by addition of 9-triptyl chloride to 9-triptycylolithium. Chromatography on silica gel,

followed by crystallization from acetone, gave crystals suitable for X-ray analysis. Crystals of Tp_2CO are monoclinic, space group $A2/a$, and contain solvent of crystallization. There are two independent molecules in the unit cell, which contains a total of 12 molecules. One set of eight molecules occupies the eight general positions in the unit cell, while the remaining four molecules are located on twofold rotation axes, with the rotation axis passing through the carbonyl carbon and oxygen atoms. The molecule of C_2 symmetry has only one independent Tp moiety, and the atoms are primed in the table of atomic parameters (Table I) and in the stereoview (Figure 1, top). The molecule of C_1 symmetry has two independent Tp moieties, and the atom numbers are unprimed in Table I and in the stereoview (Figure 1, bottom). The observation of two independent structures (C_1 - and C_2 - Tp_2CO) with significantly different conformations in the same unit cell provides support for our description³ of the gearing trajectory, as will be discussed in the next section.

The hydrocarbon, Tp_2CH_2 , was synthesized by double addition of benzyne to bis(9-anthryl)methane^{4a} and crystallized from methylene chloride. Crystals of Tp_2CH_2 are monoclinic, space group $P2_1/c$, and contain solvent of crystallization. There are two independent molecules, C_1 - and C_1' - Tp_2CH_2 , which occupy eight general positions in the unit cell and whose conformations closely resemble those of C_1 - Tp_2CO and of the previously described^{3b} Tp_2CHOH . In general, the standard deviations for the unprimed atoms are smaller than those for the primed atoms (Table II); from this circumstance and the significant distortions of the thermal ellipsoids in the primed molecule we place greater reliance on the values for C_1 - Tp_2CH_2 . A stereoview of this molecule is shown in Figure 2.

The inclusion of solvent of crystallization (acetone in the case of Tp_2CO and methylene chloride in the case of Tp_2CH_2) had previously been noted^{3b} for Tp_2CHOH (pentane-ether). Evidently, the formation of inclusion compounds is a characteristic property of this class of compounds, and is reminiscent of the tendency toward inclusion compound formation among other polyaryl systems containing three or more aryl groups.⁵ Another characteristic common to the crystal structures of all three compounds

(1) (a) Princeton University. (b) Hoffmann-La Roche, Inc. (c) On leave from Chalmers University of Technology and University of Göteborg, Sweden.

(2) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26 and references therein. See also: Glaser, R.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2777.

(3) (a) Hounshell, W. D.; Johnson, C. A.; Guenzi, A.; Cozzi, F.; Mislow, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6961. (b) Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 957. (c) Johnson, C. A.; Guenzi, A.; Mislow, K. *Ibid.* **1981**, *103*, 6240. (d) Bürgi, H.-B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K. *J. Am. Chem. Soc.*, in press. (e) Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K. *Ibid.* in press.

(4) Experimental studies paralleling some of ours³ have been independently carried out by Kawada and Iwamura. See: (a) Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1980**, *45*, 2547. (b) Kawada, Y.; Iwamura, H. *J. Am. Chem. Soc.* **1981**, *103*, 958. (c) Kawada, Y.; Iwamura, H. *Tetrahedron Lett.* **1981**, *22*, 1533.

(5) MacNicol, D. D.; McKendrick, J. J.; Wilson, D. R. *Chem. Soc. Rev.* **1978**, *7*, 65 and references therein. Recca, A.; Bottino, F. A.; Libertini, E.; Finocchiaro, P. *Gazz. Chim. Ital.* **1979**, *109*, 213 and references therein.

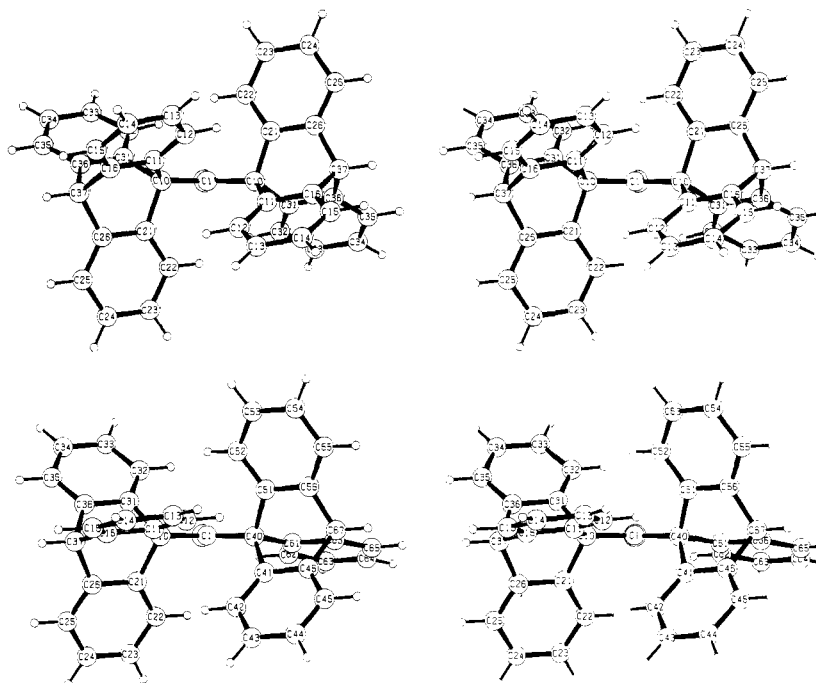


Figure 1. Stereoviews of the X-ray structures of bis(9-triptycyl) ketone (Tp_2CO); the views are down the $\text{C}=\text{O}$ axes. Top: primed molecule, C_2 symmetry. Bottom: unprimed molecule, C_1 symmetry.

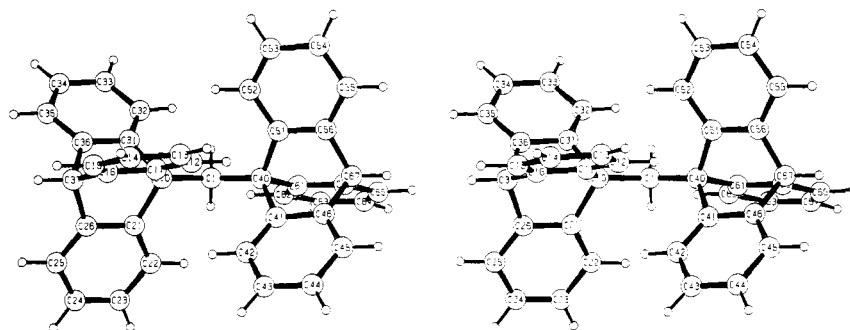


Figure 2. Stereoview of the X-ray structure of bis(9-triptycyl)methane ($C_1\text{-Tp}_2\text{CH}_2$).

is the presence of two independent molecules in the unit cell: C_1 - and C_2 - Tp_2CO , C_1 - and C_1' - Tp_2CH_2 , and C_1 - and C_1' - Tp_2CHOH .⁶ Small perturbations by the included solvent may possibly be responsible for this conformational variability.

Salient structural parameters of Tp_2CO and Tp_2CH_2 are listed in Table III, along with the corresponding X-ray parameters for Tp_2CHOH . Also listed are the corresponding parameters for Tp_2CH_2 and Tp_2CO calculated by the EFF method, using the force field from Allinger's MM2 program,⁷ with steepest descent and full-matrix Newton-Raphson geometry optimization as implemented by the program BIGSTRN-3.^{3d,8,9} As previously found^{3b} for Tp_2CHOH , the most striking feature of the X-ray structures is the greatly expanded central bond angle ($\text{C}(10)\text{-C}(1)\text{-C}(40)$), which assumes values of 128.5 and 128.8° in C_1 - and C_2 - Tp_2CO ,

respectively, and a value of 129.3° in C_1 - Tp_2CH_2 .¹⁰ The calculated (EFF) central bond angles of 130.5 and 129.6° for C_2 - and C_1 - Tp_2CO , and of 129.4° for C_1 - Tp_2CH_2 , are in excellent agreement with the experimental values. The magnitude of this angle deformation is significantly larger than that reported for systems with two *tert*-butyl (or modified *tert*-butyl) groups attached to a tricoordinate (double bonded) carbon atom^{11a} or to a tetracoordinate carbon atom.^{11b} This indicates that Tp_2CO , Tp_2CHOH , and Tp_2CH_2 , although differing in oxidation states and coordination numbers, are under considerable internal strain and distorted to the same extent.^{12,17} A feature related to the

(6) In the X-ray structure of Tp_2CHOH ,^{3b} the primed molecule represents a disordered arrangement of two molecules in the same orientation. The conformations of C_1 - and C_1' - Tp_2CHOH are quite similar, and in that respect strongly resemble C_1 - and C_1' - Tp_2CH_2 .

(7) Allinger, N. L.; Yuh, Y. H. *QCPE* 1981, 13, 395. Two modifications of this force field were used for $\text{C}_{\text{ar}}\text{-C}_{\text{ar}}$ bonds ($I^\circ = 1.3937 \text{ \AA}$ and $k_s = 8.0667 \text{ mdyn \AA}^{-1}$); cf.: Osawa, E.; Onuki, Y.; Mislow, K. *J. Am. Chem. Soc.* 1981, 103, 7475.

(8) This program is being prepared for submission to QCPE. A listing is available upon request. In the full-matrix Newton-Raphson optimization, all the elements of the $3N \times 3N$ second derivatives matrix are used. Also, all atoms are moved simultaneously, and symmetry is thus conserved.

(9) Input structures for Tp_2CH_2 and Tp_2CO had exact C_2 or C_1 symmetry. Optimization yielded stationary structures with the corresponding symmetries.⁸ Comparisons in Table III should be made between C_1 or C_1' (X-ray) and C_1 (EFF) structures and between C_2 (X-ray) and C_2 (EFF) structures.

(10) This value is well within experimental error of the value of 129.0° assumed for Tp_2CH_2 in a study of the dependence of $^{13}\text{C}\text{-}^1\text{H}$ coupling constants on C-C-C bond angles: Baum, M. W.; Guenzi, A.; Johnson, C. A.; Mislow, K. *Tetrahedron Lett.* 1982, 23, 31.

(11) From X-ray structures: (a) 125.6° (Shearer, H. M. M.; Sowerby, J. D. *J. Chem. Soc., Dalton trans.* 1973, 2629); 122.6° (Avitabile, G.; Ganis, P.; Lepore, U. *Macromolecules* 1971, 4, 239); 123.0° (Avitabile, G.; Ganis, P.; Martuscelli, E. *Acta Crystallogr., Sect. B* 1969, B25, 2378); 123.4 and 122.2° (Hall, B.; Farmer, J. B.; Shearer, H. M. M.; Sowerby, J. D.; Wade, K. J. *J. Chem. Soc., Dalton trans.* 1979, 103). (b) 126° (Bunn, C. W.; Holmes, D. R. *Discuss. Faraday Soc.* 1958, 25, 95); 125.0° (Ermer, O.; Bödecker, C.-D. *Chem. Ber.* 1981, 114, 652); 124.1 and 123.8° (Adiwidjaja, G.; Voss, J. *Chem. Ber.* 1976, 109, 761); 123.8 and 123.1° (McKinnon, B. J.; de Mayo, P.; Payne, N. C.; Ruge, B. *Nouv. J. Chim.* 1978, 2, 91); 122.6° (Benedetti, E.; Pedone, C.; Allegra, G. *Macromolecules* 1970, 3, 16).

(12) The observation of greatly expanded bond angles in bis(triphenylmethyl) ether (127.9°)¹³ and sulfide (119.8°)¹⁴ suggests that the space-demanding properties of trityl and Tp groups are comparable in magnitude. Accordingly, it is safe to predict that Tp_2Se ,¹⁵ Tp_2O ,^{4a} and 1,1,1,3,3,3-hexaphenylpropane¹⁶ also exhibit exceptionally large central C-X-C angles.

Table I. Final Atomic Parameters for $\text{Tp}_2\text{CO}^{a-c}$

atom	x	y	z
O(1)	0.3402 (2)	0.5529 (1)	0.2800 (1)
O(1)'	0.7500	0.7145 (2)	0.5000
C(1)	0.2952 (2)	0.5764 (2)	0.2405 (1)
C(10)	0.2512 (2)	0.6437 (2)	0.2464 (1)
C(11)	0.1796 (2)	0.6801 (2)	0.2030 (1)
C(12)	0.1400 (2)	0.6621 (2)	0.1530 (1)
C(13)	0.0784 (3)	0.7030 (2)	0.1198 (1)
C(14)	0.0542 (3)	0.7627 (2)	0.1355 (2)
C(15)	0.0915 (2)	0.7810 (2)	0.1855 (2)
C(16)	0.1539 (2)	0.7405 (2)	0.2187 (1)
C(21)	0.3225 (2)	0.6972 (2)	0.2690 (1)
C(22)	0.4095 (2)	0.6905 (2)	0.2773 (1)
C(23)	0.4651 (2)	0.7423 (2)	0.2985 (2)
C(24)	0.4365 (3)	0.8008 (2)	0.3121 (2)
C(25)	0.3501 (3)	0.8086 (2)	0.3041 (1)
C(26)	0.2943 (2)	0.7573 (2)	0.2828 (1)
C(31)	0.2131 (2)	0.6354 (2)	0.2886 (1)
C(32)	0.2074 (3)	0.5775 (2)	0.3139 (1)
C(33)	0.1755 (3)	0.5813 (2)	0.3524 (2)
C(34)	0.1490 (3)	0.6408 (2)	0.3652 (2)
C(35)	0.1537 (3)	0.6990 (2)	0.3398 (2)
C(36)	0.1856 (2)	0.6960 (2)	0.3019 (1)
C(37)	0.1989 (2)	0.7565 (2)	0.2735 (1)
C(40)	0.2887 (2)	0.5398 (2)	0.1924 (1)
C(41)	0.3026 (2)	0.5830 (2)	0.1508 (1)
C(42)	0.3262 (2)	0.6499 (2)	0.1531 (1)
C(43)	0.3353 (3)	0.6805 (2)	0.1118 (2)
C(44)	0.3237 (3)	0.6444 (3)	0.0691 (2)
C(45)	0.3012 (3)	0.5764 (2)	0.0667 (1)
C(46)	0.2901 (2)	0.5470 (2)	0.1073 (1)
C(51)	0.1993 (2)	0.5070 (2)	0.1683 (1)
C(52)	0.1329 (3)	0.5074 (2)	0.1861 (2)
C(53)	0.0547 (3)	0.4783 (2)	0.1585 (2)
C(54)	0.0428 (3)	0.4463 (2)	0.1137 (2)
C(55)	0.1111 (3)	0.4432 (2)	0.0966 (2)
C(56)	0.1878 (2)	0.4735 (2)	0.1234 (2)
C(61)	0.3533 (2)	0.4799 (2)	0.1995 (1)
C(62)	0.4208 (2)	0.4603 (2)	0.2415 (1)
C(63)	0.4733 (2)	0.4078 (2)	0.2387 (2)
C(64)	0.4597 (3)	0.3743 (2)	0.1949 (2)
C(65)	0.3922 (3)	0.3934 (2)	0.1525 (2)
C(66)	0.3396 (2)	0.4460 (2)	0.1546 (1)
C(67)	0.2667 (3)	0.4739 (2)	0.1097 (1)
C(1)'	0.7500	0.6538 (3)	0.5000
C(10)'	0.6670 (2)	0.6202 (2)	0.4641 (1)
C(11)'	0.6379 (2)	0.5489 (2)	0.4737 (1)
C(12)'	0.6709 (2)	0.5102 (2)	0.5165 (1)
C(13)'	0.6335 (3)	0.4487 (2)	0.5194 (2)
C(14)'	0.5633 (3)	0.4262 (2)	0.4802 (2)
C(15)'	0.5294 (2)	0.4646 (2)	0.4376 (2)
C(16)'	0.5658 (2)	0.5261 (2)	0.4346 (1)
C(21)'	0.6743 (2)	0.6178 (2)	0.4115 (1)
C(22)'	0.7437 (2)	0.6390 (2)	0.4002 (2)
C(23)'	0.7402 (3)	0.6342 (2)	0.3512 (2)
C(24)'	0.6682 (3)	0.6087 (2)	0.3140 (2)
C(25)'	0.5986 (3)	0.5880 (2)	0.3252 (1)
C(26)'	0.6022 (2)	0.5937 (2)	0.3741 (1)
C(31)'	0.5848 (2)	0.6632 (2)	0.4553 (1)
C(32)'	0.5760 (3)	0.7193 (2)	0.4824 (2)
C(33)'	0.4961 (3)	0.7500 (2)	0.4688 (2)
C(34)'	0.4259 (3)	0.7264 (2)	0.4296 (2)
C(35)'	0.4347 (2)	0.6698 (2)	0.4037 (1)
C(36)'	0.5134 (2)	0.6392 (2)	0.4166 (1)
C(37)'	0.5301 (2)	0.5756 (2)	0.3920 (1)

^a Standard deviations in parentheses. ^b Anisotropic thermal parameters and final atomic parameters for hydrogen and solvent atoms are given in the Supplementary Material. ^c Atom names for C_1 - and C_2 - Tp_2CO are unprimed and primed, respectively.

central angle expansion is the appreciable deviation of the threefold axis in the Tp moiety from the Tp-C(1) bond axis: the tilt of

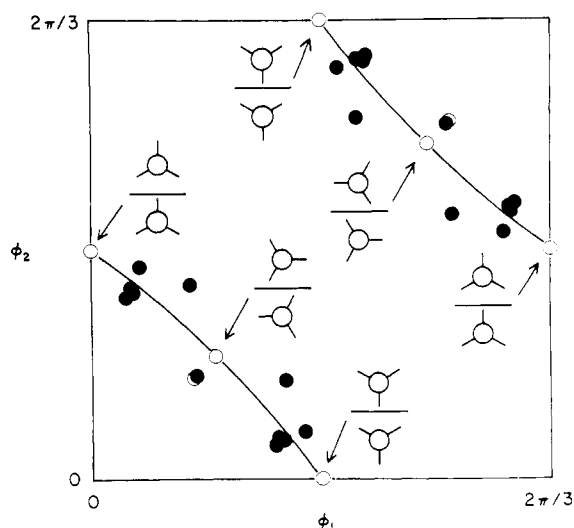


Figure 3. Conformational map of torsional coordinates (ϕ_1 and ϕ_2) for X-ray (filled circles) and calculated (open circles) structures of Tp_2X (Table III) and schematic representations³ of C_1 and C_2 conformations. Solid lines show the calculated gearing trajectory of Tp_2CH_2 .

the Tp groups out and away from the crowded, internal region of the molecule is 9.2 and 11.5° for C_1 - and C_2 - Tp_2CO , respectively, and 12.8° for C_1 - Tp_2CH_2 .^{19,20}

The accord between calculated and found values for the central bond lengths (C(1)-C(10) and C(1)-C(40)) in C_2 - Tp_2CO is also satisfactory. It is somewhat less so for the C_1 conformations, perhaps because these structures have only approximate C_2 symmetry (Figures 1 and 2).^{21,22} It is noteworthy that C(1)-C(10) in the C_1 conformations is appreciably longer than C(1)-C(40), i.e., 1.566 vs. 1.531 Å in C_1 - Tp_2CO (as compared to 1.515 Å for acetone²³), 1.578 vs. 1.532 Å in C_1 - Tp_2CH_2 , and 1.596 vs. 1.536 Å in C_1 - Tp_2CHOH . This stretching of the C(1)-C(10) bond appears to be the result of strain introduced by the compression of C(12)-H, which is part of the Tp moiety containing C(10), against the opposing notch (C(40)-C(41)-C(46)-C(67)-C(56)-C(51)) in the other Tp rotor (Figures 1 and 2; Figure 3 in ref 3b).²⁴ Replacement of the hydrogen atom on C(12) by a methyl group would obviously make the strain even more intolerable, and this qualitative conclusion is borne out by our study of gearing processes in bis(1,4-dimethyl-9-triptycyl)methane.^{3c,e}

(16) Schlenck, W.; Bornhardt, C. *Liebigs Ann. Chem.* **1912**, 394, 183. Müller, E.; Moosmayer, A.; Rieker, A. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1963**, 18B, 982.

(17) The deformation of the central angle in Tp_2CO is also reflected in a low value (1693.5 cm^{-1}) for the carbonyl stretching frequency, which is similar to that found for di-*tert*-butyl ketone (1685.8 cm^{-1}). Empirical relationships between carbonyl stretching frequencies and bond angles in strained systems have been proposed.¹⁸

(18) See, for example: Brauman, J. I.; Laurie, V. W. *Tetrahedron* **1968**, 24, 2595. Halford, J. O. *J. Chem. Phys.* **1956**, 24, 830.

(19) Tilt angles are calculated as follows. Two planes are defined for the three aromatic carbons attached to each bridgehead atom which is bonded to the central carbon, i.e., one from C(11), C(21), C(31) and the other from C(41), C(51), C(61). The angle between the vectors normal to each plane is calculated and compared to the central bond angle. The difference is the tilt angle of the triptycyl moieties away from an axis along the bridgehead atom-central carbon bond.

(20) Tilt angles are 8.1 and 13.9° for C_1 - and C_1' - Tp_2CHOH . These values are comparable to tilt angles of 11.5 and 18.0° for bis(triphenylmethyl) ether and sulfide, respectively.¹² The tilt angles found for various calculated Tp_2X structures are in good agreement with the X-ray values.

(21) The absence of special positions with mirror symmetry in the space groups $A2/a$ and $P2_1/c$ excludes the presence of molecules with exact C_2 symmetry.

(22) Discrepancies between values of parameters in Table III calculated for C_2 - Tp_2CO and C_2 - Tp_2CH_2 and found for the corresponding C_1 structures are largely due to this deviation of the X-ray structures from perfect C_2 symmetry.²¹

(23) Swalen, J. D.; Costain, C. C. *J. Chem. Phys.* **1959**, 31, 1562.

(24) Intermolecular contacts of a similar nature have been observed for 9-(2-chloroethyl)triptycene: Karle, I. L.; Estlin, J. A. Z. *Kristallogr.* **1969**, 128, 371.

(13) Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978**, B34, 696.

(14) Jeffrey, G. A.; Robbins, A. *Acta Crystallogr., Sect. B* **1980**, B36, 1820.

(15) Wittig, G.; Tochtermann, W. *Liebigs Ann. Chem.* **1962**, 660, 23.

Table II. Final Atomic Parameters for $\text{Tp}_2\text{CH}_2^{\text{a-c}}$

atom	x	y	z	atom	x	y	z
C(1)	0.4682 (6)	0.3285 (6)	0.6824 (7)	C(1)'	0.8735 (7)	0.3875 (6)	0.5967 (9)
C(10)	0.4832 (6)	0.3951 (5)	0.7374 (7)	C(10)'	0.9197 (6)	0.3533 (6)	0.5501 (8)
C(11)	0.4228 (7)	0.4317 (6)	0.7593 (7)	C(11)'	0.8979 (7)	0.2873 (6)	0.4994 (8)
C(12)	0.3503 (7)	0.4153 (6)	0.7339 (7)	C(12)'	0.8378 (7)	0.2491 (7)	0.4816 (8)
C(13)	0.3029 (7)	0.4547 (6)	0.7580 (8)	C(13)'	0.8297 (8)	0.1901 (7)	0.4322 (8)
C(14)	0.3306 (8)	0.5127 (6)	0.8069 (8)	C(14)'	0.8746 (8)	0.1693 (7)	0.3969 (9)
C(15)	0.4028 (7)	0.5305 (6)	0.8320 (7)	C(15)'	0.9365 (8)	0.2081 (7)	0.4164 (9)
C(16)	0.4471 (6)	0.4911 (6)	0.8079 (7)	C(16)'	0.9475 (8)	0.2661 (7)	0.4653 (8)
C(21)	0.5168 (6)	0.4507 (6)	0.6968 (8)	C(21)'	0.9967 (7)	0.3412 (6)	0.6163 (9)
C(22)	0.5301 (6)	0.4451 (7)	0.6194 (8)	C(22)'	1.0248 (9)	0.3494 (6)	0.7077 (11)
C(23)	0.5663 (7)	0.4988 (8)	0.5973 (8)	C(23)'	1.1030 (15)	0.3364 (10)	0.7526 (12)
C(24)	0.5871 (6)	0.5537 (7)	0.6465 (9)	C(24)'	1.1519 (14)	0.3201 (16)	0.7163 (23)
C(25)	0.5765 (6)	0.5596 (6)	0.7244 (8)	C(25)'	1.1200 (10)	0.3105 (9)	0.6291 (17)
C(26)	0.5429 (6)	0.5079 (6)	0.7478 (7)	C(26)'	1.0490 (8)	0.3205 (6)	0.5806 (10)
C(31)	0.5469 (6)	0.3834 (6)	0.8300 (7)	C(31)'	0.9270 (7)	0.4024 (7)	0.4809 (9)
C(32)	0.5837 (7)	0.3250 (6)	0.8622 (9)	C(32)'	0.8941 (7)	0.4635 (8)	0.4523 (10)
C(33)	0.6427 (8)	0.3258 (7)	0.9446 (10)	C(33)'	0.9088 (11)	0.5010 (9)	0.3895 (14)
C(34)	0.6650 (7)	0.3847 (9)	0.9910 (8)	C(34)'	0.9635 (15)	0.4746 (12)	0.3587 (13)
C(35)	0.6270 (7)	0.4432 (7)	0.9581 (8)	C(35)'	1.0011 (9)	0.4155 (10)	0.3880 (11)
C(36)	0.5686 (7)	0.4425 (6)	0.8770 (8)	C(36)'	0.9812 (9)	0.3788 (8)	0.4494 (9)
C(37)	0.5270 (7)	0.5041 (5)	0.8315 (7)	C(37)'	1.0122 (9)	0.3123 (8)	0.4811 (11)
C(40)	0.3951 (6)	0.2945 (5)	0.6298 (7)	C(40)'	0.8041 (7)	0.3593 (6)	0.6146 (8)
C(41)	0.3341 (7)	0.3342 (6)	0.5594 (7)	C(41)'	0.8118 (8)	0.2919 (6)	0.6586 (8)
C(42)	0.3388 (7)	0.3999 (7)	0.5405 (8)	C(42)'	0.8712 (8)	0.2484 (7)	0.6842 (9)
C(43)	0.2810 (8)	0.4306 (6)	0.4770 (10)	C(43)'	0.8619 (11)	0.1879 (8)	0.7242 (10)
C(44)	0.2197 (8)	0.3945 (8)	0.4307 (8)	C(44)'	0.8073 (11)	0.1695 (9)	0.7430 (11)
C(45)	0.2170 (7)	0.3255 (8)	0.4502 (9)	C(45)'	0.7518 (9)	0.2139 (9)	0.7188 (9)
C(46)	0.2736 (7)	0.2960 (7)	0.5148 (8)	C(46)'	0.7513 (8)	0.2728 (7)	0.6756 (8)
C(51)	0.3587 (7)	0.2578 (6)	0.6836 (8)	C(51)'	0.7342 (7)	0.3600 (6)	0.5373 (9)
C(52)	0.3849 (7)	0.2578 (6)	0.7747 (9)	C(52)'	0.7228 (8)	0.3780 (7)	0.4516 (11)
C(53)	0.3464 (10)	0.2222 (8)	0.8142 (9)	C(53)'	0.6563 (10)	0.3777 (9)	0.3878 (10)
C(54)	0.2835 (10)	0.1854 (7)	0.7672 (12)	C(54)'	0.5950 (9)	0.3611 (7)	0.4053 (10)
C(55)	0.2576 (7)	0.1851 (6)	0.6755 (9)	C(55)'	0.6039 (8)	0.3415 (7)	0.4907 (11)
C(56)	0.2979 (7)	0.2209 (6)	0.6351 (9)	C(56)'	0.6735 (8)	0.3431 (6)	0.5540 (8)
C(61)	0.4085 (7)	0.2346 (5)	0.5751 (7)	C(61)'	0.7917 (7)	0.4077 (6)	0.6805 (8)
C(62)	0.4800 (7)	0.2187 (6)	0.5724 (7)	C(62)'	0.8326 (7)	0.4630 (7)	0.7224 (9)
C(63)	0.4796 (8)	0.1646 (7)	0.5157 (8)	C(63)'	0.8154 (7)	0.5012 (6)	0.7822 (9)
C(64)	0.4194 (9)	0.1310 (6)	0.4690 (8)	C(64)'	0.7563 (9)	0.4810 (7)	0.8002 (8)
C(65)	0.3507 (7)	0.1465 (6)	0.4748 (8)	C(65)'	0.7118 (7)	0.4255 (8)	0.7595 (9)
C(66)	0.3465 (7)	0.1986 (6)	0.5277 (7)	C(66)'	0.7332 (7)	0.3902 (6)	0.6996 (8)
C(67)	0.2791 (6)	0.2238 (6)	0.5380 (7)	C(67)'	0.6922 (7)	0.3274 (7)	0.6510 (9)

^a Standard deviations in parentheses. ^b Atom names for C_1 - and C_1' - Tp_2CH_2 are unprimed and primed, respectively. ^c Anisotropic thermal parameters and final atomic parameters for hydrogen and solvent atoms are given in the Supplementary Material.

Table III. Comparison of Selected Experimental and Calculated Structural Parameters of Tp_2X ($\text{X} = \text{CH}_2, \text{CHOH}, \text{CO}$)^a

parameters ^b	experimental (X-ray)						calculated (EFF)			
	$\text{Tp}_2\text{CH}_2^{\text{c}}$		$\text{Tp}_2\text{CHOH}^{\text{d}}$		Tp_2CO		$\text{Tp}_2\text{CH}_2^{\text{e}}$		Tp_2CO	
	C_1	C_1'	C_1	C_1'	C_1	C_2	C_s	C_2	C_s	C_2
bond angles										
C(10)–C(1)–C(40)	129.3	(129.5)	128.9	129.1	128.5	128.8	129.4	130.2	130.5	129.6
bond lengths										
C(1)–C(40)	1.532	(1.609)	1.536	1.568	1.531	1.546	1.543	1.554	1.542	1.539
C(1)–C(10)	1.578	(1.557)	1.596	1.587	1.566	1.546	1.566	1.554	1.546	1.539
torsion angles										
C(10)–C(1)–C(40)–C(41)	54.3	(52.3)	56.1	52.2	48.8	26.8	63.7	33.2	61.2	27.1
C(10)–C(1)–C(40)–C(51)	–75.3	(–76.7)	–68.3	–75.1	–72.6	–96.3	–63.7	–92.1	–61.2	–96.5
C(10)–C(1)–C(40)–C(61)	171.7	(167.6)	179.0	175.3	170.1	150.2	180.0	155.3	180.0	148.7
C(40)–C(1)–C(10)–C(11)	10.8	(9.9)	13.9	27.6	10.5	26.8	0.0	33.2	0.0	27.1
C(40)–C(1)–C(10)–C(21)	–114.2	(–113.6)	–112.2	–100.0	–113.7	–96.3	–122.7	–92.1	–123.9	–96.5
C(40)–C(1)–C(10)–C(31)	133.2	(130.4)	134.9	148.8	135.3	150.2	122.7	155.3	123.9	148.7
ϕ_1	50.2	(47.7)	55.6	50.8	48.8	26.9	60.0	32.1	60.0	26.4
ϕ_2	9.9	(8.9)	12.2	25.5	10.7	26.9	0.0	32.1	0.0	26.4

^a Bond lengths in angstroms, angles in degrees. ^b Same numbering as in Figure 1. ^c Values for C_1' - Tp_2CH_2 (parenthesized) are considered less reliable than those for C_1 - Tp_2CH_2 . See text. ^d Reference 3b. The numbering of atoms is the same as in Figure 1. ^e Reference 3d.

Structures along the Gearing Trajectory. Previous EFF studies of Tp_2CH_2 , using MM2 in conjunction with BIGSTRN-3,^{3c,d} revealed a C_2 ground state and a gearing transition state of C_s symmetry ca. 0.2 kcal mol^{–1} higher in energy. According to these calculations, the potential energy hypersurface is virtually flat along

the gearing coordinate. Prior to the present work these conclusions had been supported only by negative evidence: no barriers to gearing have been detected in low-temperature NMR experiments^{3,4} on Tp_2CH_2 , Tp_2O , Tp_2CHOH , bis(2,3-dimethyl-9-triptycyl)methane, and Tp_2CO (Experimental Section). However,

the coexistence of two independent structures, one of C_2 and the other of approximate C_s symmetry, in the unit cell of Tp_2CO clearly implies that these conformations cannot differ appreciably in energy. This observation therefore provides the first experimental support for the prediction³ that the ground and gearing transition states in such systems differ only slightly in energy. This conclusion is borne out by examination of the eigenvalues and eigenvectors of the second derivatives matrix⁸ for Tp_2CO , which shows that the C_2 structure is an energy minimum and the C_s structure a transition state only 1.9 kcal mol⁻¹ higher in energy²⁵. Gearing is therefore a very facile process.

The calculated and experimentally determined torsion angles in Table III provide further information on the shape of the potential energy hypersurface. The torsional coordinates²⁶ used to describe the torsion of the two Tp rotors are

$$\phi_1 = (\omega_1 + \omega_2 + \omega_3)/3$$

$$\phi_2 = (\omega_4 + \omega_5 + \omega_6)/3$$

where ω_1 , ω_2 , and ω_3 are the three torsion angles terminating at C(10), and ω_4 , ω_5 , and ω_6 are the three torsion angles terminating at C(40) (Table III).²⁷ These torsional coordinates are shown on a conformational map (Figure 3), along with a line for the calculated^{3d} dynamic gearing trajectory of Tp_2CH_2 .²⁸ The trajectory is the path of minimum energy between two conformations, and the scatter of points around this line gives some indication of the breadth of the potential energy valley for the gearing pathway.²⁹ Thus, the structural correlation between the two independent parameters (ϕ_1 and ϕ_2) maps a minimum-energy region in the torsional space.^{30,31}

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. NMR spectra were recorded on a JEOL FX-90Q or (for variable-temperature ¹H NMR spectra) on a Varian XL-100 spectrometer, both operating in the Fourier transform mode. Chemical shifts are in ppm downfield from tetramethylsilane as internal reference. Infrared spectra were recorded on a Digilab FTS-20C spectrometer, operating in the Fourier transform mode. Mass spectra were measured on an AEI MS-9 high-resolution mass spectrometer, with an ionizing voltage of 70 eV. Melting points were measured in a Mel-Temp or a Thomas-Hoover apparatus, in sealed capillary tubes, and are corrected. Benzene was dried by distillation from calcium hydride. Dry ethyl ether (Mallinckrodt) was used without further purification.

Bis(9-triptycyl) Ketone (Tp_2CO). A 2.4 M solution of *n*-butyllithium in hexane (0.3 mL, 0.7 mmol) was added dropwise to an ice-cold solution of 9-bromotriptycene (0.21 g, 0.6 mmol), mp 239–244 °C (lit.³² mp 246–248 °C), in 30 mL of 2:1 dry ethyl ether/dry benzene under dry nitrogen. After 1 h of stirring at room temperature, a solution of 9-triptycyl chloride (0.20 g, 0.6 mmol), mp 186–190 °C (lit.³³ mp 193–194 °C), in dry benzene was added and the reaction mixture was stirred for

12 h. After the mixture was partitioned with saturated ammonium chloride solution, the dried (MgSO_4) extracts were evaporated under reduced pressure. The yellow residue was chromatographed on silica gel, eluant 9:1 petroleum ether (30–60 °C)/ethyl ether. The product was recrystallized from acetone by slow evaporation to give a sample suitable for X-ray crystallography: mp 375–379 °C dec; MS *m/e* (rel intensity) 534 (65), 516 (5), 506 (5), 281 (21), 253 (100); MS (high resolution) *m/e* 534.1960 ± 0.0027 (534.1984 calcd for $\text{C}_{41}\text{H}_{26}\text{O}$); IR ν_{max} [²H] trichloromethane 1693.5 cm⁻¹ (C=O); ¹H NMR (89.55 MHz) [²H]-trichloromethane (ambient temperature) δ 7.58 (dd, 6 H), 7.46 (dd, 6 H), 7.00 (dt, 6 H), 6.75 (dt, 6 H), 5.43 (s, 2 H), 2.16 (s, acetone, 29%); ¹³C{¹H} NMR (22.5 MHz) in [²H]trichloromethane δ 210.4 (CO), 206.9 (acetone CO), 146.0, 143.7 (quaternary aromatic carbons), 126.5, 125.6, 124.5, 123.6 (protonated aromatic carbons), 70.6 (quaternary aliphatic carbon), 52.2 (tertiary aliphatic carbon), 29.7 (acetone, CH₃). The appearance of the ¹H NMR spectrum remained unchanged down to -90 °C ([²H₂]dichloromethane solution). Anal. Calcd for $\text{C}_{41}\text{H}_{26}\text{O}$: ¹/₃ $\text{C}_3\text{H}_6\text{O}$: C, 91.05; H, 5.09. Found: C, 90.61; H, 5.57.

Bis(9-triptycyl)methane (Tp_2CH_2). prepared according to the literature,^{4a} had mp 412–420 °C dec (lit.^{4a} mp 416 °C). Crystals (needles) suitable for X-ray analysis were obtained by slow evaporation of a methylene chloride-methanol solution: ¹H NMR (89.55 MHz in [²H]trichloromethane, ambient temperature) δ 7.57 (dd, 6 H), 7.46 (dd, 6 H), 6.99 (dt, 6 H), 6.78 (dt, 6 H), 5.48 (s, 2 H), 5.28 (s, CH₂Cl₂, 67%), 4.86 (s, 2 H); ¹³C{¹H} NMR (22.5 MHz) in [²H]trichloromethane δ 146.2, 146.2 (quaternary aromatic carbons), 125.2, 124.9, 124.4, 123.5 (protonated aromatic carbons), 55.3 (quaternary aliphatic carbon), 55.3 (tertiary aliphatic carbon), 25.8 (secondary aliphatic carbon). Anal. Calcd for $\text{C}_{41}\text{H}_{28}$: ⁷/₈ CH_2Cl_2 : C, 84.53; H, 5.04; Cl, 10.43. Found: C, 85.04; H, 4.95; Cl, 10.22.

Crystallography. Crystals of Tp_2CO are monoclinic, space group $A2/a$, with $a = 16.760$ (3), $b = 19.885$ (3), $c = 28.738$ (5) Å, $\beta = 111.56$ (1)°, and $d_{\text{calcd}} = 1.239$ g cm⁻³ for $Z = 12$ ($\text{C}_{41}\text{H}_{26}\text{O} \cdot 1/3 \text{C}_3\text{H}_6\text{O}$, $M_r = 554.02$). Crystals of Tp_2CH_2 are monoclinic, space group $P2_1/c$, with $a = 19.717$ (7), $b = 20.001$ (5), $c = 16.590$ (6) Å, $\beta = 112.23$ (2)°, and $d_{\text{calcd}} = 1.255$ g cm⁻³ for $Z = 8$ ($\text{C}_{41}\text{H}_{28} \cdot 1/2 \text{CH}_2\text{Cl}_2 \cdot 1/2 \text{H}_2\text{O}$ assumed, $M_r = 572.15$). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu K α radiation, θ - 2θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.15 × 0.20 × 0.9 mm for Tp_2CO and 0.08 × 0.10 × 0.5 mm for Tp_2CH_2 ; the data for Tp_2CH_2 were corrected for absorption ($\mu = 13.5$ cm⁻¹). A total of 5993 (Tp_2CO) and 5658 (Tp_2CH_2) independent reflections were measured for $\theta < 57^\circ$ (Tp_2CO) and $< 48^\circ$ (Tp_2CH_2), of which 4780 (Tp_2CO) and 3217 (Tp_2CH_2) were considered to be observed ($I > 2.5\sigma(I)$). The structures were solved by a multiple-solution procedure³⁴ and were refined by block-diagonal least squares in which the matrix was partitioned into two (Tp_2CO) or three (Tp_2CH_2) blocks.

In the crystal of Tp_2CO , solvent of crystallization, presumed to be acetone, was found disordered about the twofold axes. The disordered orientation of an acetone molecule was described by five carbon atoms, three on the twofold axis and two off, which were refined isotropically. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms (except the solvent 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 indices are $R = 0.056$ and $wR = 0.074$ for the 4780 observed reflections. The final difference map has no peaks greater ± 0.4 e Å⁻³. Final atomic parameters are listed in Table I, selected parameters are listed in Table III, and stereoviews of the X-ray structures are shown in Figure 1.

For Tp_2CH_2 , a difference map calculated after isotropic refinement of the 82 carbon atoms had several peaks on it which were attributed to solvent atoms. Six peaks were assumed to be due to disordered methylene chloride. Five of these peaks were designated as chlorine atoms and one as carbon; all were assigned multipliers of one half. A seventh, isolated peak was considered to be an oxygen atom of a water (or methanol) molecule.³⁵ In the final refinement, anisotropic thermal parameters were used for the 82 carbon atoms of the two Tp_2CH_2 molecules and isotropic temperature factors were used for the hydrogen atoms and the seven atoms representing solvent. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.093$ and $wR = 0.086$ for the 3217 observed reflections. The largest peaks on the final difference map, none of which exceed ± 0.6 e Å⁻³, are in the vicinity of the disordered solvent

(25) When the two X-ray structures were used as input geometries, both relaxed to the C_2 form. No other stationary structures were discovered along the gearing pathway.

(26) Murray-Rust, P.; Bürgi, H.-B.; Dunitz, J. D. *Acta Crystallogr., Sect. A* 1979, **A35**, 703.

(27) In the general case, $\phi_1 = (\omega_1 + \omega_2 + \omega_3 - 2\pi)/3$ and $\phi_2 = (\omega_4 + \omega_5 + \omega_6 - 2\pi)/3$, where $\omega_j < \omega_{j+1} < \omega_{j+2}$ and $0 \leq \omega_j < 2\pi/3$ ($j = 1, 4$).

(28) The symmetry of the ϕ_1 , ϕ_2 torsional space in Figure 3 demands that the general points (x, y) , (y, x) , $(-x + 2\pi/3, -y + 2\pi/3)$, and $(-y + 2\pi/3, -x + 2\pi/3)$ represent isometric structures. Thus, each molecule of C_1 symmetry corresponds to four points in Figure 3.

(29) The breadth of the valley suggests that each Tp group may undergo some libration or independent motion, somewhat in the manner of slightly worn gears, rather than the strictly concerted motion described by the calculated trajectory.

(30) Dunitz, J. D. "X-ray Analysis and the Structure of Organic Molecules"; Cornell University Press: Ithaca, NY, 1979; p 363 ff.

(31) We have also investigated the distortion of Tp rotors in Tp_2X ($\text{X} = \text{CH}_2$, CHOH , CO) from local C_{3v} symmetry. A conformational map³⁰ with symmetry coordinates describing the bending distortions of the three torsion angles among benzene rings in each Tp shows distortion to C_s symmetry through contraction of one angle with concomitant expansion of the other two. However, the magnitude of the distortion is small ($< 10^\circ$).

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(33) Bartlett, P. D.; Greene, F. D. *J. Am. Chem. Soc.* 1954, **76**, 1088.

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

(35) The variability in the solvate content found for Tp_2CH_2 by integration of the ¹H NMR spectrum, elemental analysis, and X-ray analysis may be accounted for by loosely bound solvent molecules and disorder in the crystal.

molecules. Final atomic parameters are listed in Table II, and selected structural parameters are listed in Table III, with the less reliable values for the primed molecule in parentheses. A stereoview of the unprimed molecule is shown in Figure 2.

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Registry No. Bis(9-triptycyl) ketone, 82510-94-9; bis(9-triptycyl)-methane, 73611-46-8.

Supplementary Material Available: Structure factor tables, final anisotropic thermal parameters, atomic parameters for hydrogen and solvent atoms, bond lengths, and bond angles with standard deviations for Tp_2CO and Tp_2CH_2 (Tables IV-XIII) (49 pages). Ordering information is given on any current masthead page.

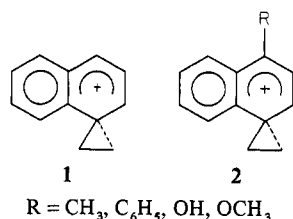
Stable Carbocations. 209.¹ α -Ethylenenaphthalenium Ions

George A. Olah* and Brij P. Singh

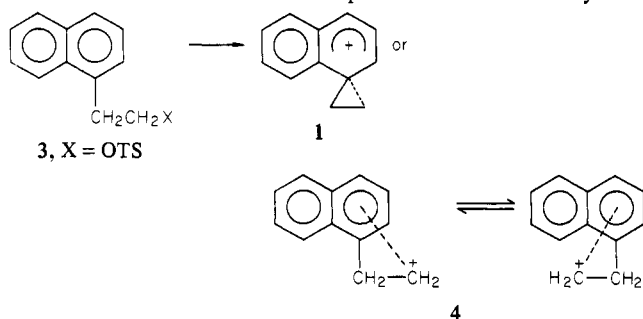
Contribution from the Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received January 8, 1982

Abstract: Ionization of 2- α -naphthylethyl chloride (5) and 2- β -naphthylethyl chloride (9) in $\text{FSO}_3\text{H-SbF}_5/\text{SO}_2\text{ClF}$ at -80°C gave the protonated naphthalenium ions 6 and 10 or the rearranged naphthylethyl cation 8, which were observed by carbon-13 and proton NMR spectroscopy. Spiro alcohol 12a under similar conditions gave only polymeric material. The 4-methyl-substituted precursor 13a on ionization gave the corresponding 4-methyl-substituted α -ethylenenaphthalenium ion 2 and a minor amount of ion 14. Ionization of phenyl-substituted spirocyclic tertiary alcohol 17 gave the corresponding ion 18. Protonation and methylation of the spiro ketone 12 led us to observe the spirocyclic ions 21 and 22 whose structures were proved by carbon-13 and proton NMR spectroscopy.

In continuation of our studies on the nature of phenylethyl cations,² we now wish to report efforts to prepare the elusive α -ethylenenaphthalenium ion 1 and the first direct observation



of its substituted homologues, that of the 4-methyl-, 4-phenyl-, 4-hydroxy-, and 4-methoxy- α -ethylenenaphthalenium ions 2, under stable ion conditions. Participation by the naphthyl group has been proposed in solvolytic studies^{3a-d} of 2- α -naphthylethyl derivatives 3. The results were interpreted in terms of α -ethylene-



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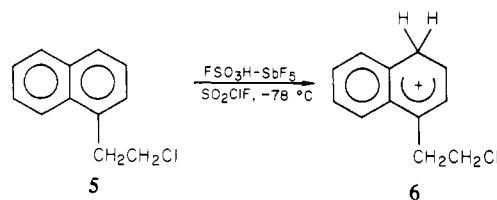
(2) (a) For discussion concerning the nomenclature of ethylenebenzenium ions, see: Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808; *Chimia* **1971**, *8*, 275; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173. (b) For recent reviews, see: Schleyer, P. v. R.; Lancelot, C. J.; Cram, D. J. "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1969; Vol. III. Story, P. R.; Clark, B. C., Jr. *Ibid.* Chapter 23. (c) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 2236; **1976**, *98*, 6304. (d) Olah, G. A.; Porter, R. D. *Ibid.* **1971**, *93*, 6877; **1970**, *92*, 7627. (e) Olah, G. A.; Comisarow, M. B.; Kim, C. J. *Ibid.* **1969**, *91*, 1458. (f) Olah, G. A.; Pittman, C. U., Jr. *Ibid.* **1965**, *87*, 3507.

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naphthalenium ion 1 or a rapidly equilibrating pair of π -bridged ions^{3c} such as 4 intermediates.

Results and Discussion

In our efforts to prepare ion 1, we added 2- α -naphthylethyl chloride (5) in SO_2ClF to a well-stirred solution of $\text{FSO}_3\text{H-SbF}_5$



$\text{SbF}_5/\text{SO}_2\text{ClF}$ at -78°C , resulting in a brownish yellow solution. The 60-MHz proton NMR spectrum of this solution at -80°C displayed absorptions at δ 4.25 (s, 4 H), 5.2 (br s, 2 H), 8.4 (m, 4 H), 8.96 (d, 1 H), and 9.53 (d, 1 H). Observation of a total of 12 protons in the spectrum shows that under the superacidic conditions protonation has taken place on the ring. The 20-MHz carbon-13 NMR spectrum of the solution displayed three absorptions in the aliphatic region, at $\delta_{13\text{C}}$ 39.6 (t), 43.0 (t), and 44.2 (t), and nine more peaks in the aromatic and also low-field region. The observation of three saturated methylene groups in the proton and carbon-13 NMR spectra clearly rules out structure 1. If the spectrum were that of the parent ion 1, it should show only two peaks in the aliphatic region of the carbon-13 NMR spectrum, one for the symmetrical cyclopropane methylenes and the other for the spiro quaternary carbon atom. The presence of three triplets in the aliphatic region of the proton-coupled carbon-13 NMR spectrum indicates ring protonation, i.e., the 4-(β -chloroethyl)-1-naphthalenium ion 6. Indeed, the proton and carbon-13 NMR chemical shifts of the observed ion 6 (Table II) are comparable to those of the previously reported⁴ 1-methylnaphthalenium ion 7. Even after being warmed to -50°C , ion 6 was found to be stable, with no indication of the formation of ion 1. On the other hand, when 2- α -naphthylethyl chloride (5) was ionized in $\text{SbF}_5/\text{SO}_2\text{ClF}$ alone at -78°C , it gave the α -

(4) Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299.