Anal. Calcd for C$_{30}$H$_{34}$N$_2$O$_5$: C, 71.69; H, 6.82; N, 5.57. Found: C, 71.77; H, 6.87; N, 5.51.

Deprotection of a 388-mg sample of this pure *N*-(*tert*-butoxy)carbonyl derivative of **19** by treatment at 0 °C with a solution of CF$_3$COOH (3 mL), CH$_2$Cl$_2$ (3 mL), and anisole (500 mg) gave, after purification on silica gel (99:1 CHCl$_3$–MeOH), 297 mg of pure **19** as a colorless powder: ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.17–7.42 (m, 12 H, ArH), 6.19–6.96 (m, 2 H, ArH), 5.03 (s, OC*H*$_2$Ph), 4.89 (dd, *J* = 5.0, 8.5 Hz, NC*H*ArH), 4.57 (AB quartet, OC*H*$_2$Ph), 4.08 (dd, *J* = 2.3, 5.4 Hz, C*H*NH$_2$), 3.95 (dd, *J* = 10.1, 8.5 Hz, C*H*HOBn), 3.76 (dd, *J* = 10.1, 5.0 Hz, CH*H*OBn), 3.45 (app t, *J* = 5.5 Hz, β C-4 H), 3.06 (dd, *J* = 2.3, 5.6 Hz, α C-4 H), 1.92 (br s, NH$_2$); IR (CHCl$_3$) 1761 cm^{-1}; MS (CI) *m/e* 403 (MH), 375.

Acknowledgment. The financial support of the National Science Foundation (CHE 82-03366 and Departmental Instrumentation grants) is gratefully acknowledged.

Stable Simple Enols. 9.[1] Solid State Structures and Conformations of Several Simple Enols and Their Keto Tautomers

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Contribution from the Department of Chemistry, Technion—Israel Institute of Technology, Haifa 32000, Israel, and The Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel. Received September 14, 1984

Abstract: The structures of the enols trimesitylethenol (**2**), (*Z*)-1,2-dimesityl-2-phenylethenol (**4**), their keto isomers **5** and **6**, the ethanolate of 1-(9-anthryl)-2,2-dimesitylethenol (**3**), and trimesitylethylene (**7**) were determined by X-ray crystallography. The structures of **2**–**4** are the first ones determined for *simple* enols, and the structural effects of crowding on bond lengths and angles are discussed. The main features of the solid-state conformations are consistent with and reinforce those found in solution as follows: (a) Compounds **2**–**7** have propeller structures where all the rings are twisted from the reference plane in the same direction, corroborating static and dynamic NMR data in solution. The torsional angles of the rings in the vinyl propellers which were compared with literature values can be correlated with the rotational barriers for the enantiomerization in solution. (b) The OH group of **2** is in a syn-periplanar conformation in the direction of the cis-β-mesityl group, while that of **3** is in anti-periplanar conformation due to hydrogen bonding to an ethanol of crystallization. This is in line with the conformational dependence of the enolic OH geometry in solution on hydrogen bonding to the solvent or to the β-mesityl group. (c) The HCCO torsional angles in **5** and **6** are 177.4° and −157.8°, in agreement with the conformation suggested from UV spectra for bulky ketones in solution. (d) The α-ArCO torsional angle in **5** is 47.7°, a value lower than for formally less bulky α-aryl ketones, but in line with UV data in solution.

Remarkable progress in the preparation and reactions, especially ketonization, of simple ions (i.e., enols substituted only by hydrogens, alkyl, or aryl groups, but not by strongly electron-withdrawing substituents such as CO, CN, SO$_2$R, etc.) has been achieved in recent years.[2–4] Structural data are available for vinyl alcohol in the gas phase from microwave[5a] and infrared spectra[5b] or from MM and MO calculations[6] and for its radical ion from photoelectron spectroscopy.[7] The conformation of the OH group in solution in relation to the double bond was deduced from ^3J(HCOH) and ^4J(HC=COH) coupling constants[2c,d,8,9] or from IR studies.[9,10] Only four structures of aryl-substituted enols were determined in the solid state by X-ray crystallography[11] but all the compounds were substituted by electron-withdrawing (e.g., C=N, C=O) groups. Even the "simplest" one, i.e., **1**,[11d] is not

1
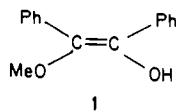
"simple" by the definition above, due to the electron-withdrawing

MeO group and to the strong intramolecular hydrogen bonding, which increase the enol stability and enable its isolation.

(1) Part 8: Biali; S. E., Rappoport, Z. *J. Am. Chem. Soc.*, in press.

(2) (a) Blank, B.; Fischer, H. *Helv. Chim. Acta* **1973**, *96*, 506. (b) Ripoll, J. L. *Nouv. J. Chim.* **1979**, *3*, 195. (c) Capon, B.; Rycroft, D. S.; Watson, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 724. (d) Capon, B.; Rycroft, D. S.; Watson, T. W.; Zucco, C. *J. Am. Chem. Soc.* **1981**, *103*, 1761.

(3) Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 6122. Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *Ibid.* **1984**, *106*, 460. Chiang, Y.; Kresge, A. J.; Wirz, J. *Ibid.* **1984**, *106*, 6392.

(4) For reviews, see: (a) Hart, H. *Chem. Rev.* **1979**, 513. (b) Hart, H.; Sasaoka, M. *J. Chem. Educ.* **1980**, *57*, 685.

(5) (a) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399. (b) Hawkins, M.; Andrews, L. *J. Am. Chem. Soc.* **1983**, *105*, 2523.

(6) (a) Bouma, W. J.; Radom, L. *J. Mol. Struct.* **1978**, *43*, 267. (b) Bouma, W. J.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1977**, *99*, 6443. (c) Nobes, R. H.; Radom, L.; Allinger, N. L. *J. Mol. Struct. Teochem.* **1981**, *85*, 185. (d) Dodziuk, H.; v. Voithenberg, H.; Allinger, N. L. *Tetrahedron* **1982**, *38*, 2819.

(7) Albrecht, B.; Allan, M.; Haselbach, E.; Neuhaus, L.; Carrupt, P.-A. *Helv. Chim. Acta* **1984**, *67*, 216.

(8) (a) Capon, B.; Siddhanta, A. K. *Tetrahedron Lett.* **1982**, *23*, 3199. (b) Capon, B.; Siddhanta, A. K. *J. Org. Chem.* **1984**, *49*, 80.

(9) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641.

(10) (a) Rodebush, W. H.; Feldman, I. *J. Am. Chem. Soc.* **1946**, *68*, 896. (b) Buswell, A. M.; Rodebush, W. H.; Whitney, R. McL. *Ibid.* **1947**, *69*, 770.

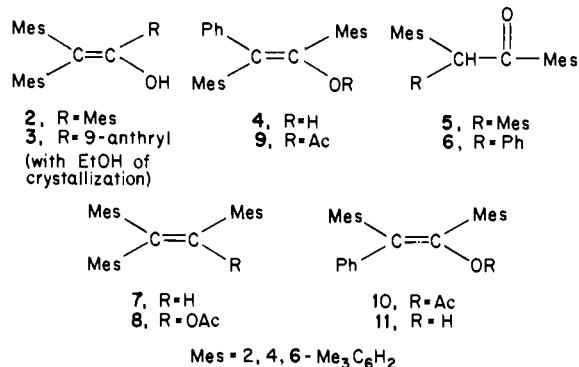† Technion—Israel Institute of Technology.
‡ The Hebrew University of Jerusalem.

Table I. Bond Lengths (Å) and Angles (deg) for Triarylvinyl Systems

parameter[a]	2A	2B	3	4[b]	7
C(1)–C(2)	1.362 (7)	1.343 (7)	1.339 (6)	1.26 (1)	1.343 (3)
C(1)–Ar^3	1.489 (7)	1.492 (7)	1.477 (6)	1.561 (8)	1.480 (4)
C(2)–Ar^1	1.496 (7)	1.506 (7)	1.500 (6)	1.508 (8)	1.497 (4)
C(2)–Ar^2	1.503 (7)	1.508 (7)	1.507 (6)	1.546 (7)	1.517 (4)
C(1)–X	1.366 (6)	1.403 (7)	1.382 (5)	1.454 (9)	0.98 (2)
α_1	123.2 (5)	120.9 (5)	121.2 (4)	119.3 (8)	123.8 (3)
α_2	117.3 (4)	119.6 (5)	118.5 (3)	126.3 (7)	120.2 (2)
α_3	119.5 (5)	119.5 (5)	120.2 (4)	114.4 (8)	116.1 (2)
α_4	129.0 (5)	130.2 (5)	128.0 (4)	126.8 (9)	131.1 (3)
α_5	108.8 (4)	110.2 (5)	113.3 (4)	113.2 (7)	113 (1)
α_6	122.1 (5)	119.5 (5)	118.8 (4)	120 (1)	115 (1)
ϕ_1	52.5	51.4	58.2	38.3	52.9
ϕ_2	54.6	58.2	56.9	74.4	59.3
ϕ_3	52.7	55.0	62.5	79.0	54.4
θ^c	8.3	7.6	−2.1	1.1	4.8

^{a} For the definitions of the α's and ϕ's, see structure **14**. ^{b} Data for the main crystallographic form are given. ^{c} Twist coordinate of the double bond.

The conformations,[9,12,13] the equilibria with the carbonyl tautomers,[14,15] and the static and dynamic NMR behavior of several crowded[16] 1,2,2-triarylethenols[12] and 2,2-diarylethenols[13] were recently studied by us in solution. The gas-phase behavior of the cation radicals of these species was also investigated.[15,17a] The crowding of the systems resulted in several unusual properties such as higher or nearly similar stabilities of the enols compared with the carbonyl isomers,[1,14,15] a frozen conformation in solution due to hindered rotation around the =C—Ar bonds at room temperature or below,[12,13] and reciprocal methyl/hydrogen transfer from an ortho position of a 1-mesityl ring to the 2-aryl group in the ion radical of 1,2,2-triarylethenols in the gas phase.[17a]

A better understanding of the solution chemistry and probably of the gas-phase chemistry of the cation radicals could be obtained if the conformations and bond lengths and angles of these enols were available. We were able to obtain crystals of these long-lived enols free from their keto isomers and to determine their structures by X-ray diffraction. Six representatives of triaryl-substituted

2, R=Mes
3, R=9-anthryl
(with EtOH of crystallization)

4, R=H
9, R=Ac

5, R=Mes
6, R=Ph

7, R=H
8, R=OAc

10, R=Ac
11, R=H

Mes = 2,4,6-Me$_3$C$_6$H$_2$

systems, i.e., the enols **2–4**, the ketones **5** and **6**, and trimesityl-

ethylene **7**, were chosen for the following reasons:

(1) We wished to verify unequivocally the enolic structures and that of **5**, since data on stable enols are not available and **5** was prepared only recently[1] after previous unsuccessful attempts.

(2) They could be used to determine whether the enol obtained as a single product by addition of MesMgBr to mesityl phenyl ketene[16] has the Z (**4**) or the E (**11**) geometry, and to compare its structure with those of the acetates **9** and **10**.[18]

(3) We wanted to obtain the C=C and the C—O bond lengths for the enols for use in MM calculations on these systems.[19] The effect of the α-OH group on the bond lengths could hopefully be deduced by comparing **2**, **7**, and the acetate **8**[12] or of **4** and its acetate **9**.[18] Comparison of **2**, **3**, and **8** or of **2** and **4** should give information on the effects of the α-substituents and β-aryl groups. These parameters will be compared with those for the less crowded 2,2-dimesitylethenols[20] in a future publication.

(4) The dynamic behavior of **2** and **3** and the dependence of the flip route and enantiomerization barrier on the bulk of the aryl substituents were ascribed to a chiral propeller conformation in solution.[12] A direct corroboration of this conformation from the solid-state data and a possible correlation between the torsional angles of the aryl groups and the flip route are important for understanding the rotational behavior of vinyl propellers. Moreover, since certain triarylvinyl-X systems are biologically active (e.g., tamoxiphene)[21] and the propeller geometry may be relevant to the geometry of the receptor,[22] we wanted to find out how general this geometry is.

(5) The conformation of the OH group in solution is solvent dependent. In a non-hydrogen bond accepting solvent the conformation is syn-periplanar **12**, probably due to π(Ar^2)···OH
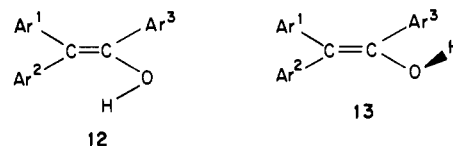
bonding, while in a strong hydrogen bond accepting solvent it is anti-clinal **13**. We were interested if the same effects would be also observed in the solid state.

(6) It was of interest to see whether the unusual reciprocal CH$_3$/H transfer in the gas phase is due to an especially short

(11) Search of the Cambridge Structural Database up to 1982 gave only the first three structures. (a) Kalyanaraman, A. R.; Srinivasan, R. *Ind. J. Pure Appl. Phys.* **1971**, *9*, 215. (b) Fuess, H.; Lindner, H. J. *Chem. Ber.* **1975**, *108*, 3096. (c) Semmingsen, D. *Acta Chem. Scand., Ser. B* **1977**, *B31*, 114. (d) McGarrity, J. F.; Cretton, A.; Pinkerton, A. A.; Schwarzenbach, D.; Flack, H. D. *Angew. Chem. Suppl.* **1983**, 551; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 405.

(12) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477.

(13) (a) Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 3357. (b) Nugiel, D. A.; Rappoport, Z. *Ibid.*, in press.

(14) Rappoport, Z.; Biali, S. E. 6th IUPAC Conference on Physical Organic Chemistry, Louvain la Neuve, Belgium, July 11–16, 1982. Abstract: Rappoport, Z.; Biali, S. E. *Bull. Soc. Chim. Belg.* **1982**, *91*, 388. Rappoport, Z., The 50th Anniversary Meeting of The Israel Chemical Society, The Hebrew University of Jerusalem, April 10–12, 1984; Abstr. p 31.

(15) Biali, S. E.; Lifshitz, C.; Rappoport, Z.; Karni, M.; Mandelbaum, A. *J. Am. Chem. Soc.* **1981**, *103*, 2896.

(16) E.g.: (a) Fuson, R. C.; Armstrong, L. J.; Kneisley, J. W.; Shenk, W. J. *J. Am. Chem. Soc.* **1944**, *66*, 1464. (b) Fuson, R. C.; Chadwick, D. H.; Ward, M. L. *Ibid.* **1946**, *68*, 389. (c) For other references, see ref 9 in ref 12.

(17) (a) Biali, S. E.; Depke, G.; Rappoport, Z.; Schwarz, H. *J. Am. Chem. Soc.* **1984**, *106*, 496. (b) Biali, S. E.; Rappoport, Z.; Depke, G.; Eckart, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Proc.* **1985**, *63*, 289.

(18) (a) Biali, S. E.; Rappoport, Z., unpublished results. (b) Recent crystal structures of several triarylethylenes (Gilbert, J.; Miguel, J. F.; Précigoux, G.; Hospital, M.; Raynaud, J. P.; Michel, F.; Paulet, C. *J. Med. Chem.* **1983**, *26*, 693) gave torsional angles of 38–58° for the aryl groups, values within the range of Table III.

(19) Biali, S. E.; Meyer, A. Y.; Rappoport, Z.; Yuh, Y. H., submitted for publication.

(20) Kaftory, M.; Nugiel, D. A.; Biali, S. E.; Rappoport, Z., unpublished results.

(21) Précigoux, G.; Courseille, C.; Geoffre, S.; Hospital, M. *Acta Crystallogr., Sect. B* **1979**, *B35*, 3070.

(22) Hospital M.; Busetta, A.; Courseille, C.; Précigoux, G. *J. Steroid Biochem.* **1975**, *6*, 221.

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Table II. Relevant Bond Lengths and Angles for the Triarylethanones **5** and **6**

bond length, Å	5	6	angle, deg	5	6	torsional angle, deg	5	6
O–C(1)	1.212 (9)	1.214 (7)	C(1)–C(2)–C(3)	102.6 (7)	118.4 (4)	C(4)–C(3)–C(2)–H	25.6	–60.3
C(1)–C(2)	1.53(1)	1.531 (8)	C(1)–C(2)–C(9)	119.2 (6)	107.6 (4)	C(8)–C(3)–C(2)–H	–156.1	116.5
C(1)–C(18)	1.521 (9)	1.518 (8)	C(3)–C(2)–C(9)	116.0 (6)	114.4 (4)	C(10)–C(9)–C(2)–H	60.6	–22.3
C(2)–C(3)	1.52 (1)	1.532 (8)	C(2)–C(1)–C(18)	118.8 (6)	116.2 (5)	C(14)–C(9)–C(2)–H	–115.2	159.6
C(2)–C(9)	1.55 (1)	1.533 (6)	O–C(1)–C(2)	122.0 (6)	122.1 (5)	H–C(2)–C(1)–O	177.4	–157.8
C(2)–H	1.02 (6)	0.89 (4)	O–C(1)–C(18)	119.0 (6)	121.6 (5)	O–C(1)–C(18)–C(19)	–133.3	111.3
			C(3)–C(2)–H	108 (3)	96 (2)	O–C(1)–C(18)–C(23)	47.7	–66.6
			C(1)–C(2)–H	111 (3)	111 (2)			
			C(9)–C(2)–H	100 (3)	109 (2)			

distance between the α-o-Me group and the ipso position of the β-ring in the neutral species.

(7) The conformations of triarylethanones were never investigated. We recently showed that the conjugation between the α-Ar and the CO moieties in **5** and **6** is higher than in less crowded ketones such as MesCOMe.[1] We wanted to corroborate this in the solid state and to obtain the torsional angles of the aryl rings and the HCCO moiety in the ketones.

(8) The relative stabilities of the enols compared with the isomeric ketones are connected with the steric bulk of the aryl group. Space-filling molecular models show that both species are extremely hindered, but since the models overestimate steric effects[23] we wanted to compare the **2/5** and **4/6** enol/keto pairs, in order to see whether the much higher stability of **2** compared to **5**, vs. that of **4** compared to **6**, is due to nonbonded repulsions which are revealed in the solid-state conformation.

Results and Discussion

Structural Commentary. Important bond lengths and angles for the substituted triarylethylenes **2, 3, 4,** and **7** are given in Table I and for the triarylethanones **5** and **6** in Table II. Other bond lengths and angles are deposited as supplementary material Tables S1–S12, and atomic coordinates, structure factors, and anisotropic vibrational tensors for the six compounds in the supplementary material, Tables S13–S30 (for details see the end of the paper). The numbering of the enols is given in Figure 1 and of the ketones in Table II. Stereoviews of the various molecules are shown in Figures 2–7.

Trimesitylethenol (**2**) crystallizes with two crystallographically independent molecules (**2A** and **2B**) in the asymmetric unit.

2,2-Dimesityl-1-(9-anthryl)ethenol (**3**) crystallizes with one ethanol molecule. Although the heavy atoms of the ethanol molecule were found to suffer from large thermal motion, the OH hydrogen atom of the EtOH was detected in a difference Fourier map. The solvent molecule forms hydrogen bonds with the hydroxyl groups of two enol moieties thus forming a tetramer which consists of two enol molecules and two ethanol molecules around a center of inversion (stereoview is shown in Figure 8).

1,2-Dimesityl-2-phenylethenol (**4**) was found to be disordered at the ethylene portion. The disorder is described as two molecules related to each other by a rotation of 90° of the double bond (occupation factors are 0.74 and 0.26). Similar disorder was observed in tetraisopropylethylene[24] and in α,α'-dimethylstilbene.[25]

Structure Corroboration. The crystallographic data for the enols **2–4** and for the ketone **5** serve as unequivocal evidence for their
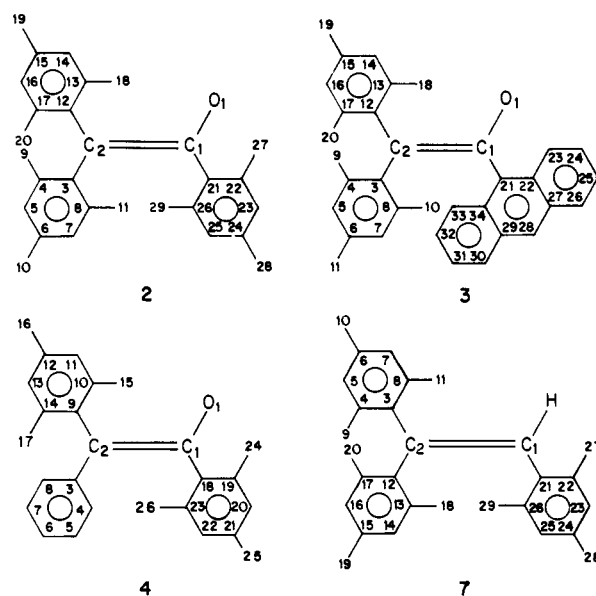

Figure 1. Numbering scheme for **2–4** and **7**.

structure. This is necessary, since although the NMR and IR evidence is in line with the structures, isomeric structures cannot be unequivocally excluded. Since ketone **5** could not be previously obtained, and its UV spectrum is somewhat unusual,[1] the present data eliminate all the possible reservations that could have been raised concerning its structure.

The structure of Fuson's 1,2-dimesityl-2-phenylethenol[16a] was now established as that of the Z isomer **4**. This has a mechanistic importance since its acetylation with Ac₂O/pyridine gives one acetate, whereas acetylation of its magnesium enolate gives another acetate.[16a] The two acetates were identified by us as **9** and **10**, respectively.[18]

Two points are pertinent to the following discussion. First, the refinement of most of the compounds, especially **4**, is not good enough to discuss small differences in the geometrical parameters. Second, we will assume that gross features of the structural data in the solid are applicable for analyzing related structural and conformational questions in solution. We have no assurance that this is the case and that crystal packing forces[26] do not change significantly parameters such as torsional angles. Nevertheless, when possible we will discuss the similarities between the crystal and the solution data for the parameters investigated.

(23) Blount, J. F.; Finocchiaro, P.; Gust, D.; Mislow K. *J. Am. Chem. Soc.* **1973**, *95*, 7019.

(24) Casalone, G.; Pilati, T.; Simonetta, M. *Tetrahedron Lett.* **1980**, 2345.

(25) Calle, G.; Busetti, V.; Galiazzo, G. *Cryst. Struct. Commun.* **1981**, *10*, 867.

(26) (a) Bernstein, J.; Hagler, A. T. *J. Am. Chem. Soc.* **1978**, *100*, 673. (b) Kitaigorodsky, A. J. *Chem. Soc. Rev.* **1978**, *7*, 133.
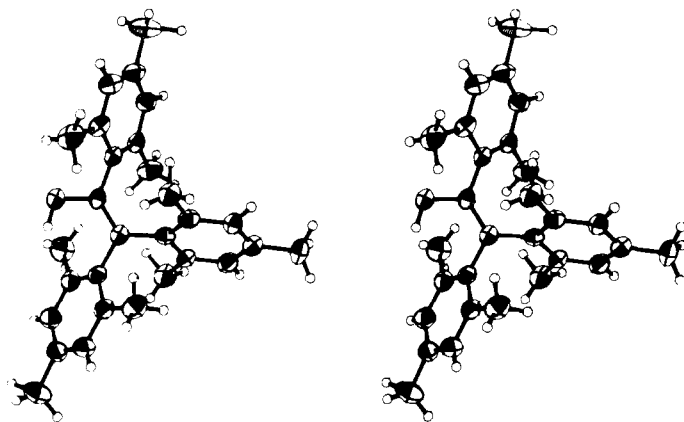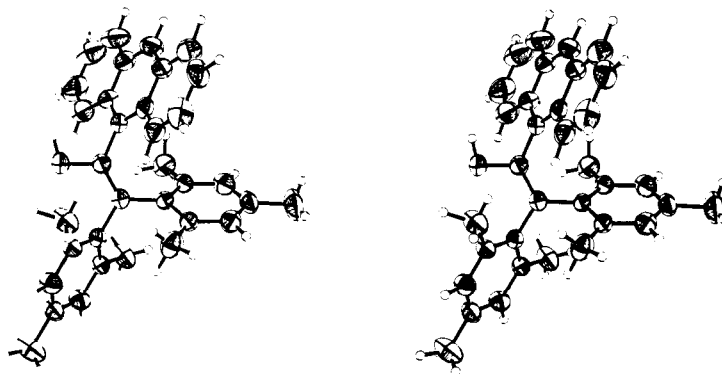
Figure 2. Stereoscopic view of **2**.

Figure 3. Stereoscopic view of **3**.
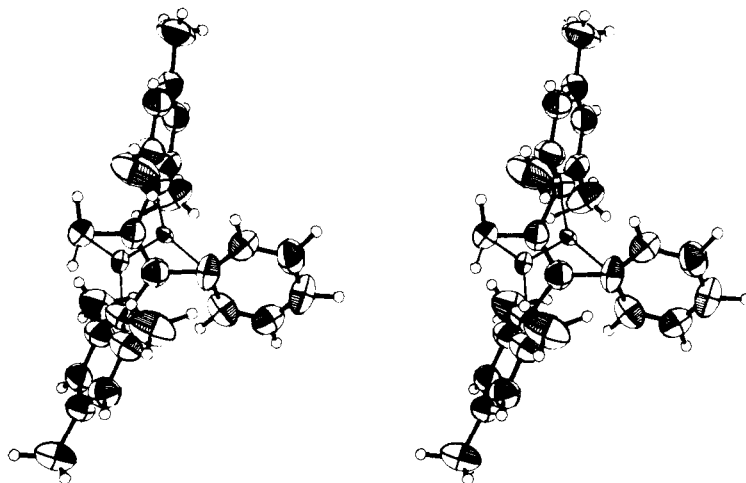
Figure 4. Stereoscopic view of **4**.
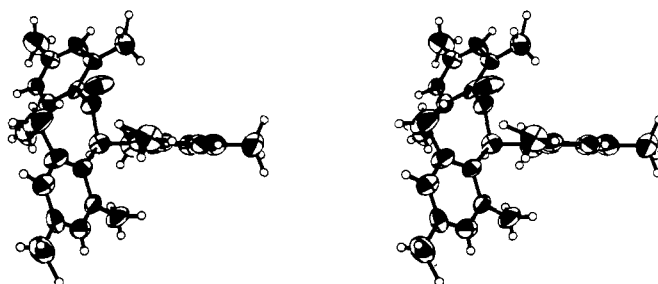
Figure 5. Stereoscopic view of **5**.

Propeller Conformations of Triarylethenols and Other Tri-arylvinyl Systems. An important structural feature is related to the hydrocarbon skeleton of the enols. Inspection of the torsional angles of Table I and Figures 2–4 and 7 shows that in each case the three aryl rings are rotated in the same sense from the plane of the double bond, giving an helical propeller conformation. In order to probe the generality of this phenomenon we analyzed the structures of all the triarylethylenes, triarylvinyl–X, and 2,2-di-

Figure 6. Stereoscopic view of **6**.

Figure 7. Stereoscopic view of **7**.

Figure 8. Stereoscopic view of the tetramer arrangement in the crystal of **3**·EtOH.
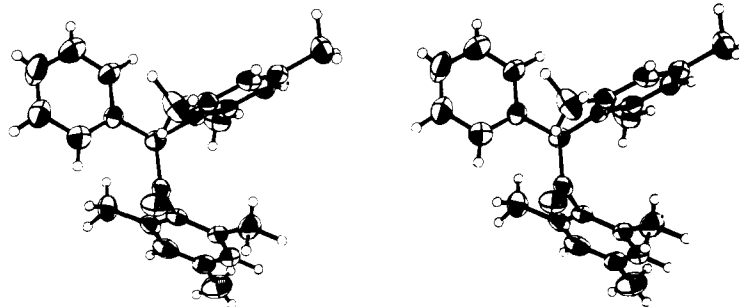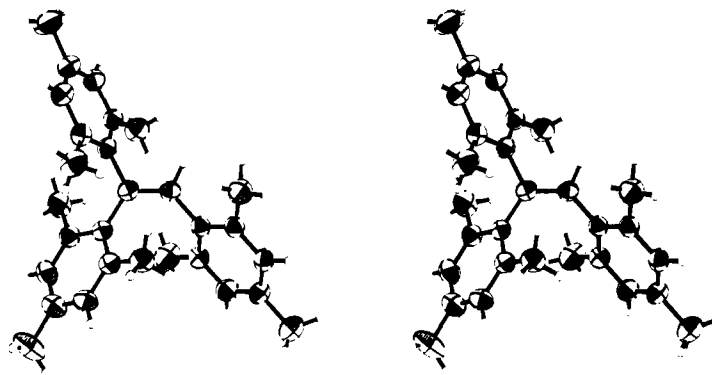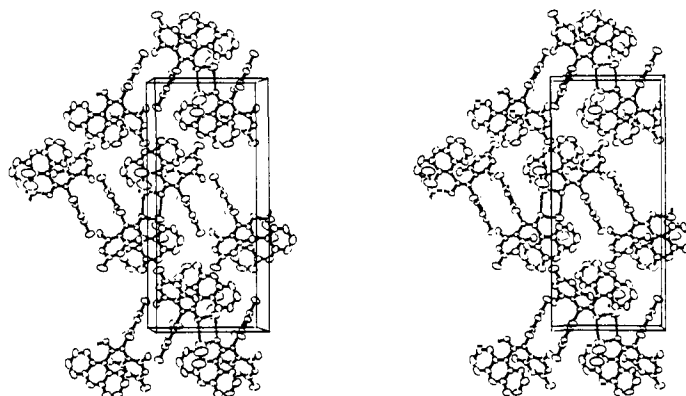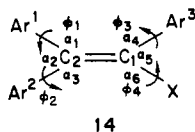
arylvinyl–X systems for which crystallographic data were available up to 1982 in the Cambridge Structural Database. The data for the 1,1-diarylvinyl propellers will be given in a future work.[20] The values for 15 triarylvinyl systems (including one which was determined twice and two unpublished values[18]) and for two tetraarylethylenes are collected in Table III. The torsional angles ϕ_1, ϕ_2, ϕ_3, and ϕ_4 are defined in structure **14**.

<center>

Ar^1 ϕ_1 ϕ_3 Ar^3

α_1 α_4

α_2C$_2$ ══ C$_1$ α_5

α_3 α_6

Ar^2 ϕ_2 ϕ_4 X

14
</center>

Without a single exception, all the 52 structures[27] have a

propeller arrangement of the aromatic rings around the double bond.[38] If this arrangement is singularly present in compounds having different rings, different substituents, and different environments in the crystal it is an unavoidable conclusion that it represents the minimum energy conformation for the polyarylvinyl systems. This seems to be a special case of a wider generalization since extensive work on the Ar$_3$X and Ar$_3$XY systems indicated

(27) Different crystal conformations and different determinations of the same structure were counted separately.

(28) Kilbourn, B. T.; Owston, P. G. *J. Chem. Soc. B* **1970**, 1.

(29) Hunter, D. H.; Payne, N. C. *Can. J. Chem.* **1983**, *61*, 421.

(30) Ernst, S.; Hite, G. *Acta Crystallogr., Sect. B* **1976**, *B32*, 291.

(31) Fournies-Marquina, J. M.; Courseille, C.; Busetta, B.; Hospital, M. *Cryst. Struct. Commun.* **1972**, *1*, 261.

(32) Bertolasi, V.; Gilli, G. *Cryst. Struct. Commun.* **1978**, *7*, 517.

(33) Barrans, Y.; Précigoux, G.; Hospital, M.; Sekera, A.; Miquel, F. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2271.

(34) Kaftory, M.; Apeloig, Y.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1985**, 29.

(35) Wanigasekera, D.; Lee, C. C.; Houminer, Y.; Aviv, M.; Rappoport, Z. *J. Org. Chem.* **1984**, *49*, 4367.

(36) Blount, J. F.; Mislow, K.; Jacobus, J. *Acta Crystallogr., Sect. A* **1972**, *A28*, 812.

(37) Hoekstra, A.; Vos, A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1716.

(38) In principle, the minimum energy path for the helicity reversal process in the triarylvinyl propellers could be deduced from the distribution of the torsional angles of the various structures ("the structural correlation method": Burgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153) as shown by Dunitz and co-workers for the stereoisomerization of triphenylphosphine oxide (Bye, E.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 5893). However, we could not apply it for the tri- and tetraarylvinyl systems due to the small number of experimental points. In contrast, for diarylvinyl systems, where only two degrees of freedom are present, a picture consistent with the experimental results was obtained by using a combination of data from MO calculations[39] and the structural correlation method.[20]

(39) Stegemeyer, H.; Rapp, W. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 1165.

Table III. Literature Bond Lengths and Angles for Tri- and Tetraarylvinyl Systems

	Ar¹	Ar²	Ar³	X	ref code[a]	l, Å	α_1, deg	α_2, deg	α_3, deg	α_4, deg	α_5, deg	α_6, deg	ϕ_1, deg	ϕ_2, deg	ϕ_3, deg	ref
1	Ph	DMEP[b]	Ph	Et	APPBH[c]	1.323	122.6	113.7	123.6	121.8	113.2	124.9	51.9	51.7	54.8	28
2	Ph	DMEP[b]	Ph	Et	APPBH[c]	1.329	123.1	112.9	123.9	123.7	114.5	121.8	46.0	59.7	50.6	28
3	DMEP[b]	Ph	Ph	Et	TTAMOX	1.347	123.6	113.8	122.6	122.6	115.3	122.5	47.0	54.3	63.6	21
4	Ph	DMEP[b]	p-IC₆H₄	Et		1.342	122.9	114.3	122.8	122.2	114.5	123.3	49	59	57	29
5	DMEP[b]	Ph	p-IC₆H₄	Et		1.340	125.3	112.7	122.0	123.3	114.1	122.6	51	63	45	29
6	DEEP[d]	Ph	Ph	Cl	CLOMCL[e]	1.303	120.3	115.0	124.6	126.2	112.9	120.8	51.4	53.1	55.8	30
7	p-EtC₆H₄	Ph	Ph	Br	BEPPET	1.324	121.9	115.3	122.8	126.9	112.8	120.3	39.7	49.6	62.1	31
8	Ph	An[f]	Ph	C(=S)NHC₆H₁₁-c	HTPTAC	1.368	124.1	113.6	122.2	124.4	114.6	121.0	58.2	47.4	40.5	32
9	An[f]	Ph	Ph	CN	MXPACN	1.361	122.3	115.8	121.9	125.8	114.3	119.8	41.4	45.3	47.6	33
10	Ph	An[f]	An[f]	Br		1.314	121.9	115.1	123.0	128.7	111.8	119.5	46.9	68.6	47.6	34
11	Anthr[g]	Anthr[g]	An[f]	Br		1.350	121.5	114.1	124.3	126.5	111.5	122.0	42.1	44.1	75.6	34
12	Anthr[g]	Anthr[g]	An[f]	OTs		1.339	120.7	114.0	124.9	128.9	113.1	117.9	43.4	41.0	44.4	34
13	An[f]	Tol[h]	An[f]	Br		1.33	120.9	115.9	123.1	127.6	112.9	119.5	58.8	76.3	44.8	35
14	Mes	Ph	Mes	OAc		1.33	121.5	115.6	122.7	130.6	112.5	116.4	65.4	57.8	65.4	18
15	Ph	Mes	Mes	OAc		1.33	121.6	115.8	122.5	128.0	115.0	116.7	43.0	76.6	69.6	18
16	Mes	Mes	Mes	OAc		1.33	124	117	119	128.1	114	117	57	64	59	12
17	Mes	Mes	Mes	Mes	MESETY	1.364	122.8	114.4	122.8	122.8	114.4	122.8	54.6	54.6	54.6[i]	36
18	Ph	Ph	Ph	Ph	TPHETY	1.355	123.0	115.4	121.6	125.0	113.9	121.1	43.8	47.3	43.8[j]	37

[a]Reference code in the Cambridge Structural Database. [b]DMEP = p-Me₂NCH₂CH₂OC₆H₄. [c]Crystal structure of the HBr salt. The two structures differ in the conformation of the DMEP group. [d]DEEP = p-Et₂NCH₂CH₂OC₆H₄. [e]Crystal structure of the HCl salt. [f]An = p-MeOC₆H₄. [g]Anthr = O=CAr¹Ar³C = 10-Anthronylidene. [h]Tol = p-MeC₆H₄. [i]ϕ_4=54.6°. [j]ϕ_4=56.0°.

that they also exist in a propeller conformation.[40]

The torsional angles of the three enols and of trimesitylethylene (Table I; ϕ_1 = 38.3–58.2°; ϕ_2 = 54.3–74.4°, ϕ_3 = 53.0–79.0°) are within the general region found for the triarylvinyl–X systems of Tables III (ϕ_1 = 39.7–65.4°; ϕ_2 = 41.0–76.3°; ϕ_3 = 40.5–75.6°). Comparison between the angles of the two forms of **2** is important since it gives an indication (or even a lower limit) to the effect of crystal forces on the torsion angles. The differences between the chemically equivalent torsional angles are 1.1–3.6°. The change **2 → 3**, i.e., from an α-mesityl- to an α-9-anthryl-substituted enol increases ϕ_3 by 9.8° (7.5°), ϕ_2 by 2.3° (−1.3°), and ϕ_1 by 5.7° (6.8°). However, it should be noted that the conformation of the OH group in **3** is different from that in **2** due to the presence of an EtOH molecule (see below), and its steric interaction with the mesityl group cis to it is lower in **3**, which is presumably reflected in small differences in ϕ_2. An indication that the effect of the OH group on the propeller conformation is small is given by comparing **2** and **7**. The differences are small and the lower ϕ_1 and ϕ_2 values (by 1.0° and 2.9°) for **7** than the average values for **2A** and **2B** may be within the range of combined experimental error.

Although the presence of the α-aryl group is expected to increase the torsional angles of the β-aryl rings, the effect is not very large. The torsional angles parallel to ϕ_1 and ϕ_2 in dimesityl ketone Mes₂C=C=O (where an α-substituent is absent) are 56.7° and 47.8°,[18a] whereas the values for 2,2-dimesitylethenols are 50.0° and 63.4°.[20]

A significant result is the large difference between ϕ_1 and ϕ_2 for enol **4**. The ϕ_1 value is half of the ϕ_2 value, and the latter is the highest and the former is the lowest found for our enols. Similar large differences between ϕ_1 and ϕ_2 were also found for the corresponding (Z)- and (E)-acetates **9** and **10**, where the torsional angles for the phenyl group are 22° and 32° lower than that for the β-mesityl group.

Two factors are important in determining the torsional angles. The conjugation energy between an aryl group and a C=C bond amounts to few kilocalories per mole,[41] and this factor will operate to increase the planarity of the system and to reduce the torsional angles. The steric interactions between neighboring aryl groups will increase the torsional angles since the planar form is the most crowded, as found by calculation even for the *relatively* uncrowded 1,1-diphenylethylene.[39] The torsional angles of the minimum energy conformation of 1,1-diphenylethylene were calculated to be 30°.[39] It is expected that the torsional angles will increase when the two *gem*-aryl groups are mesityls, and the experimental values given above show that the interaction between *gem*-mesityl groups increases the torsional angles to ≥50°. The higher the repulsive interaction between the β-aryl groups, the higher is the torsional angle, and hence the lower will be the effect of the α-aryl group. The steric interaction between two cis aryl groups across the double bond is significant as shown by the torsional angles of 19–66° in α-substituted *cis*-stilbene derivatives. However, when the β-aryl group is already twisted due to the presence of the other β-aryl group, the effect will be much smaller as reflected by the relatively minor change in ϕ_3 for the change **2 → 3**.

The effect of relatively non-bulky para-substituted aryl groups is best shown for compound **9** in Table III where the additional α-substituent is the small CN group. The torsional angles are 41.4–47.6°. A comparison of tetraphenylethylene[36] with tetramesitylethylene[37] is revealing. The average torsional angle for the former is 9.7° smaller than for the latter. Other trends in Table III can also be explained by similar considerations, but significant differences between the two β-aryl groups or between the α- and β-aryl groups are usually associated with the presence of a bulky α-substituent X.

(40) (a) Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535. (b) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.

(41) Planar styrene was calculated to be 4.4 kcal mol⁻¹ more stable than "perpendicular" styrene (Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1496.

(42) Tinant, T.; Touillaux, R.; Declercq, J. P.; Van Meerssche, M.; Leroy, G.; Weiler, J. *Bull. Soc. Chim. Belg.* **1983**, *92*, 101, 865.

The results for **4**, **9**, and **10** reflect a competition between electronic and steric effects. Mesityl is a better electron donor than phenyl and its conjugation with the double bond should be energetically more favored. Mesityl is also much bulkier than phenyl and for steric reasons it will tend to conjugate less than phenyl. The much higher torsional angle of the β-mesityl compared with the β-phenyl in the Mes(Ph)C$_\beta$-substituted systems indicates that the steric effect is more important.

Torsional Angles and Rotational Mechanisms. The torsional angles of the aryl groups in the triarylvinyl propellers should be connected with the rotational route for enantiomerization. The preferred conformation of **2**, **3**, and tetra-*o*-tolylethylene[43] in solution was suggested to be the propeller conformation, and the interpretation of their dynamic NMR behavior was based on this assumption. Rotational mechanisms in molecular propellers are usually discussed in terms of flip mechanisms,[40,44] in which none, one, two, three, or all the rings "flip", i.e., rotate via a plane perpendicular to the reference plane (the double-bond plane for the vinyl propellers) without edge interchange. The nonflipping rings rotate concomitantly through the reference plane.[45] It was found that for **2** and **3** the three rings move in a correlated rotation and the rotational mechanism with the lowest activation energy is the three-ring flip.[12] For the closely related **7** the lowest energy rotational mechanism is the [α,β]-two-ring flip,[18] in which the ring cis to the hydrogen passes through the double-bond plane in the idealized transition state. Two questions arise in connection with the torsional angles: (a) Can the barrier to rotation be correlated with the torsional angles of the rings? (b) Can the change in the rotational mechanism be explained by a change in the torsional angles?

In the transition state of the three-ring flip all three rings are simultaneously perpendicular to the plane of the double bond. The lower rotational barrier for **3** (16.2 kcal mol^{-1}) compared with that for **2** (18.4 kcal mol^{-1}) was therefore ascribed to two factors: a lower transition-state energy resulting from lower steric interactions since the 9-anthryl group is "thinner" than a mesityl group,[46] and a higher ground state for **3**, resulting from a higher torsional angle of the α-ring.[12] This latter feature is now corroborated since ϕ_3 in **3** (62.5°) is significantly larger than in **2** (54.1°).[38]

Similar steric arguments suggest that a change of the OH group of **2** to the H of **7** will reduce the torsional angles, lowering therefore the ground-state energy and consequently raising the rotational barrier for the three-ring flip. The barrier to the two-ring flip should simultaneously decrease since it will be sterically easier for the ring cis to the hydrogen to pass through the molecular plane. This effect is, however, not reflected in the torsional angles in the solid. For **2** (average of **2A** and **2B**) and **7** the ϕ_1 and ϕ_3 values are practically identical and ϕ_2 is larger for **7** than for **2**; the smallest angle is ϕ_1, although the expectation is that ϕ_2 will be smaller. We therefore conclude that the torsional angles in the present limited case do not reflect the observed change in the rotational mechanism.

Bond Lengths and Angles in the Ethylenes. The large scatter of the C—OH and C=C bond lengths (1.370–1.454 and 1.260–1.362 Å, respectively) seems to result from the poor structure refinement and not from being real. This is shown by the differences between the values for **2A** and **2B**, as well as by the abnormally short C=C bond and abnormally long C—O bond for **4**. The latter values may also reflect the difficulty in locating the pairs of C(1) and C(2) atoms for each one of the two molecules in the unit cell. However, the average value for the two forms is similar to the value calculated (1.35 Å) for **4** by MM.[19]

Taking into account the reasonable assumption that steric interaction between vicinal substituents will mainly result in an angle, rather than in a bond length, change, we found no correlation between bond lengths and the structure within the experimental error. E.g., the C(1)—C(2) bond of **7** is expected to be shorter than in **2** due to a possible contribution from the dipolar structure Mes$_2$C$^-$—C(=$^+$OH)Mes and a minor steric interaction between the OH and Ar^2. Likewise the C(1)—C(2) bond was expected to be longer in **3** than in **2**. The bond lengths for **3** and **7** are slightly shorter than the average of **2A** and **2B**. We note that all the values (except for **4**) are longer than the values calculated by Radom et al. (1.312,[6a] 1.339,[6b] 1.314[6c] Å) for the parent vinyl alcohol or from the value determined by X-ray diffraction (1.29 Å) for enol **1**.[11d]

It was recently concluded that "the double bond in crowded ethylenes is highly resistant to elongation: the longest recorded lengths are 1.358 ± 0.004 Å".[47] There are three values in Table III with longer C(1)–C(2) bonds than this "record", but two of them (entries 8 and 9) are for olefins with polar groups on the double bond. The only authentic case with longer bond is tetramesitylethylene (C(1)–C(2) = 1.364 Å)[36] where elongation of the bond is expected for steric reasons. This bond is longer than that in **7** with the three mesityl groups both because the steric interactions are larger and since the interaction between Ar^1 and Ar^3 is easily relieved in **7** by increasing the angle α_4.

The C–O bond lengths of **2** and **3** and the average value for the two forms of **4** (not given) are similar to the values found for phenols (1.37–1.40 Å; average 1.38 Å)[48] or for **1** (1.40 Å).[11d] There is no bond shortening due to hydrogen bonding to the EtOH moiety in **3·EtOH** or to the Ar^2 group (see below).[49]

The angles α_1–α_4 are sensitive to steric effects of both vicinal and geminal groups. The Ph—C=C angles in *trans*-stilbene are 125.8–127.0° [50a,b] whereas in *cis*-stilbene the angles are widened to 129.5° [50c] due to steric repulsion between the cis-phenyl groups. The Ar^{1}C(2)Ar^2 angle (corresponding to α_2 in our systems) is 125.1° [18] in dimesityl ketene with no substituents on C(1), while it is lower than 118° for most other 1,1-diarylethylenes studied.[20] In 2,2-dimesitylethenol the average value for four crystallographic forms is 121.1 ± 1.8° [20]

The general trend for the tri- and tetraarylvinyl systems of Table III is for closing the geminal angles α_2 (112.7–115.9° for compounds 1–13) and α_5 (111.5–115.3°) at the expense of the three ArC(1)C(2) angles α_1, α_3, and α_4. The angles of the mesityl-substituted compounds of Table I follow this trend when account is being taken of the larger bulk of the mesityl group compared with most other substituents of Table III. The α_2 values for the 1-aryl-2,2-dimesitylvinyl systems including **8** (Table III, entry 16) are consistently wider and the α_4 values are mostly wider than those for the other compounds of Table III, whereas the α_3 values are consistently smaller. The interaction between the bulky aryl groups in relieved at the expense of the angles α_3, α_5, and α_6 at the vicinity of the small (H, OH) substituent X.

Regarding flip mechanisms we expect that a wider angle between two aryl groups will reduce the barrier for the three- and two-ring flips. Comparison of **2** with **3** shows that α_1 and α_4 are wider for **2**, α_2 is smaller for **2**, and α_3 is similar in both. Comparison of **2** with **7** shows that α_1, α_2, and α_4 are wider in the latter. Due to the errors in the α values we are reluctant to conclude whether these changes affect the barriers in the predicted manner.

The presence of bulky substitutents introduces slight distortions at the double bond. The out of plane bending coordinates[51] of

(43) Willem, R.; Pepermans, H.; Hallenga, K.; Gielen, M.; Dams, R.; Giese, H. J. *J. Org. Chem.* **1983**, *48*, 1890.

(44) Kurland, R. J.; Schuster, I. I.; Colter, A. K. *J. Am. Chem. Soc.* **1965**, *87*, 2279.

(45) A schematic representation of the ideal transition states for the flip mechanisms in vinyl propellers is given in ref 12.

(46) Hine, J.; Skoglurd, M. J. *J. Org. Chem.* **1982**, *47*, 4758.

(47) Ōsawa, E.; Musso, H. *Top. Stereochem.* **1982**, *13*, 117.

(48) (a) Goldberg, I. In "The Chemistry of Functional Groups, Supplement E, The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analgoues"; Patai, S., Ed.; Wiley: Chichester, 1980; p 175. (b) Baroux, C.; Perrin, M.: Thozet, A.; Bertholon, G.; Perrin, R. "3rd European Crystallographic Meeting Abstracts"; European Committee of Crystallography: Zurich, Switzerland, 1976; p 204.

(49) A significant bond shortening due to hydrogen bonding was found for the enol form of acetylacetone by electron diffraction. 1.315 Å: Lowrey, A. H.; George, C.; D'Antonio, P.; Karle, J. *J. Am. Chem. Soc.* **1971**, *93*, 6399. 1.287 Å: Andreassen, A. L.; Bauer, S. H. *J. Mol. Struct.* **1972**, *12*, 381.

(50) (a) Bernstein, J. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1268. (b) Hoekstra, A.; Meertens, P.; Vos, A. *Ibid.* **1975**, *B31*, 2813. (c) Traettenberg, M.; Frantsen, E. M. *J. Mol. Struct.* **1975**, *26*, 69.

(51) Winkler, F. K.; Dunitz, J. D. *J. Mol. Biol.* **1971**, *59*, 169.

C(1) and C(2) range between −2.9° and 1.5° and the twisting coordinate θ is small in 3, 4, and 7 and much larger for the two forms of 2 (Table I). The value for 2 is similar to that for tetramesitylethylene[36] (Table III), but values for other, apparently less crowded, systems give similar twist angles.

Conformation of the Hydroxy Group. An extensive study of the $^3J(HCOH)$ coupling constants for $Mes_2C=CHOH$ and the $\delta(OH)$ for this enol and for 2–4 in solution indicated that the conformation of the OH group in relation to the double bond is solvent dependent.[9] The conformation is close to syn-planar (cf. 12) in non-hydrogen bond accepting solvents, but it is anti-clinal (13) with a C=C—O—H dihedral angle between 90° and 150° (which is not exactly known) in strongly hydrogen bond accepting solvents.

The crystallographic data strongly support the concept of conformational dependence on hydrogen bonding. The average C=C—O—H dihedral angle in 2 is 14.1°; i.e., the conformation is syn-periplanar with the OH group and the double bond in nearly the same plane. Due to the disorder, the same angle was not determined for 4. Luckily, since 3 crystallized with an ethanol of crystallization, the conformation of an enol with intermolecular hydrogen bonding could be determined. In 3·EtOH the OH group and the double bond are again nearly in the same plane, except that the conformation is now anti-periplanar with a C=C—O—H dihedral angle of 166° (cf. Figure 8). Unfortunately, the valuable comparison with the OH conformation in unsolvated 3 (which is expected to be syn-periplanar) could not be made since the crystals of unsolvated 3 were unsuitable for crystallographic study.

A similar anti-type conformation is obtained when the steric hindrance around the double bond is low enough to allow intermolecular hydrogen bonding between different enol molecules. It was found in the intermolecular hydrogen bonded structure of tetrameric $Mes_2C=CHOH$.[20] The differences between the anti-clinal conformation found in solution and the anti-periplanar conformation found in the crystal were discussed previously.[9]

The preference for a syn conformation in non-hydrogen bond accepting solvents was ascribed to an intramolecular $\pi(Ar)\cdots HO$ bond.[9] Crystallographic evidence for an analogous $\pi(C=C)\cdots HO$ hydrogen bonding was recently given by Dunitz et al. on the basis of nonbonding distances of 2.11 and 2.16 Å from the hydroxylic hydrogen to the two carbons of the double bond.[52] The nonbonded distances between the enolic hydrogen and the ring carbons C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, and C_{17} of Ar^2 in 2A are 2.53, 2.67, 3.63, 4.35, 4.25, and 3.23 Å, and the corresponding values in 2B are 2.30, 3.20, 4.06, 4.23, 3.56, and 2.55 Å. The distance to the β-cis ipso carbon (or to the C_{12}–C_{13} bond) in 2A is relatively short, although it is still longer than Dunitz's value.[52] A weak $\pi(Ar^2)\cdots HO$ hydrogen bonding in the solid state may be indicated.

Important Structural Features of Triarylethanones. Structural features of the ketones 5 and 6 that are relevant to their spectra, DNMR behavior, and their relationship to the isomeric enols are the C(1)–C(2) and C–C(Ar) bond lengths, the torsional angles OC(1)C(18)C(26), and HC(1)C(2)O, and the helicity of the molecules (Table II).

The C(1)—C(2) bond lengths are only slightly shorter than a carbon–carbon single bond and are appreciably longer than the C(1)—C(2) bonds in the isomeric enols 2 and 4. The C(1)—Ar^3, C(2)—Ar^1, and C(2)—Ar^2 bonds in 5 and 6 are also significantly longer than the three =C—Ar bonds in 2 and 4. Consequently, the distances between α- and β-aryl groups are longer in the ketones than in the enols.

The angles around the carbonyl group of 5 are nearly 120° and the deviation from 120° is slightly larger for 6. This could indicate that steric interaction between the substituted C(1) and C(2) moieties is not very large. There is a significant deviation in several bond angles at C(2) from the tetrahedral values. The angle between the two β-rings increases (although it is still smaller than in the enols) and one C(1)C(2)Ar angle increases to almost 120°, but these changes are not completely compensated by a decrease

in the other C(1)C(2)Ar angle. This amounts to a tendency to planarization of the C(3)C(9)C(1)C(2) unit and the hydrogen is not far from being perpendicular to this moiety.

The HC(2)C(1)CO torsional angle for 5 is very close to 180° and that for 6 deviates from 180° by ca. 22°. Consequently, the C=O and the C—H bonds are in anti relationship, Ar^3 and H are nearly eclipsed, and the carbonyl group is bisected by the bulky Ar_2CH group as in 15. A 15-type conformation for bulky ketones
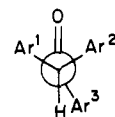
15

was suggested on the basis of UV spectra,[53] but we are unaware of any X-ray corroboration for this suggestion. A structure where the hydrogen and the C=O group are eclipsed was suggested for less bulky ketones[53] and the X-ray data clearly distinguish between these alternatives.

Other interesting angles are the $Ar^3C=O$ torsional angles. These are ca. 48° for 5 and ca. 67° for 6. An ArC=O torsional angles of 63° was calculated from the UV spectra[54] and an angle of 60–90° was estimated from the NMR by using shift reagents,[55] for the intuitivity less crowded MesCOMe. The UV spectra of 5 suggested that this angle in solution is smaller, i.e., that the conjugation between the carbonyl and the mesityl moieties is greater for 5 than for MesCOMe. This is corroborated now and the calculated angle in solution (39°) does not differ very much from the observed value in the solid. However, the value of 32° calculated for 6 in solution is much smaller than the value obtained in the solid in the present work and we have no explanation for this.

In contrast to torsional angles of the enols which are usually defined in relation to the double-bond plane, the presence of the sp^3-hybridized C(2) enables definition of the torsional angles of the other two rings relative to different reference planes. In Table II the torsional angles of the β-rings are given in relation to the HC(2)C(ipso)C(Ar) atoms. For both ketones one torsional angle is relatively small (22–26°) and the other large (ca. 60°), but the important point is that the torsional angles of the three rings are all in the same direction, as shown by their signs. Consequently, the molecules have a distorted propeller shape and are chiral. Indeed, the NMR of 5 at low temperature shows pairs of diastereotopic *o*-Me groups and *meta* hydrogens for the α-ring and is consistent with a pair of rapidly interconverting enantiomeric propeller conformations.[1] Its dynamic NMR behavior was interpreted on this basis.[1]

Crowding in the Enols and Ketones. Steric interactions between neighboring bulky aryl (especially mesityl) groups are clearly responsible for unusual phenomena observed for our compounds. These include the high thermodynamic stabilities of the enols 2 and 4 compared with the keto forms 5 and 6,[1,14,15] the high kinetic barriers to ketonization and enolization of 2 and 4–6 in solution, and the reciprocal Me/H transfer from an α-*o*-methyl group to the ipso position of a β-aryl group in their radical ions.[17]

Relevant nonbonded distances for the reciprocal Me/H transfer for our compounds were given and briefly discussed in our previous work[17] and will not be repeated here. The kinetic barrier to the enol ketonization could be understood if C(2) is shielded from the approach of a proton, which is one of the steps for the ketonization process. Relevant nonbonded distances between the *o*-substituents A–F (= H, Me) and between them and C(2) are given in Table IV. For example, in 2A the six *o*-methyl groups form two triangles above and below C(2) with nonbonded distances to C2 ranging from 2.995 to 4.066 Å and 3.555 to 5.738 Å within the triangles. These short contacts are in the usual range of the

(52) Schweizer, W. B.; Dunitz, J. D.; Pfund, R. A.; Ramos Tombo, G. M.; Ganter, C. *Helv. Chim. Acta* **1981**, *64*, 2738.

(53) Dubois, J.-E. *Pure Appl. Chem.* **1977**, *49*, 1029.
(54) Braude, E. A.; Sondheimer, F. *J. Chem. Soc.* **1955**, 3754.
(55) Abraham, R. J.; Bergen, H. A.; Chadwick, D. J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1161.

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Table IV. Relevant Nonbonded Distances in **2-7**
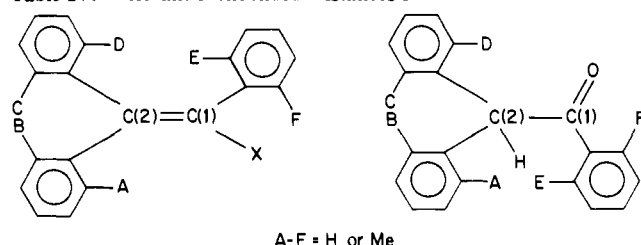
A-F = H or Me

dist	2A	2B	3	4	5	6	7
C(2)–A	3.042	2.968	2.954	3.055	2.814	2.959	3.032
C(2)–B	2.998	3.039	3.069	2.829	3.200	3.057	2.985
C(2)–C	2.995	3.054	3.071	2.482	2.949	2.652	2.991
C(2)–D	3.051	3.001	2.987	2.880	3.073	2.786	3.044
C(2)–E	3.253	4.052	3.440	3.392	3.193	3.256	3.341
C(2)–F	4.066	3.282	2.760	3.721	4.082	3.950	3.949
A–C	3.643	3.669	3.451	3.236	3.830	3.594	3.532
A–E	4.038	5.738	4.501	3.921	4.843	4.566	4.242
C–E	3.639	3.555	3.292	4.115	4.319	6.051	3.942
B–D	3.688	3.599	3.538	3.934	4.072	3.694	3.635
B–F	5.681	3.931	3.188	4.265	5.537	4.883	5.246
D–F	3.582	3.789	2.933	3.319	5.148	5.651	3.739

sum of the van der Waals radii. Consequently, approach of an electrophile such as a proton to C(2) is hindered, resulting in a kinetic barrier to both the acid-catalyzed and the base-catalyzed ketonization. We also predict that the rates of other electrophilic reactions on C(2), e.g., bromination, would also be severely reduced compared with those for less crowded olefins.

The bond angles around C(2) in the ketones close up compared with the enols due to the hybridization change $sp^2 \rightarrow sp^3$. Although C(1) does not undergo a parallel hybridization change, as a result of decreased steric interactions between the aryl groups bonded to C(1) and C(2) the three bond angles around C(1) tend to become equal (Table II). In both ketones one aryl group on C(2) (phenyl in **6** and mesityl in **5**) is coplanar with the C(1)–C(2) bond while the second aryl group is almost perpendicular (–81.0° in **6** and 88.2° in **5**). The third aryl group is rotated by 71.1° in **6** and by 52.7° in **5**, and the difference of ca. 20° reflects the lower crowding near a phenyl compared with a mesityl group.

It is difficult to ascribe the difference in stability of at least 3 kcal mol^{-1} between **2** and **5** to any specific unfavorable interaction in **5**. The average C(2)–Me distances for **2A**, **2B**, and **5** are identical and the standard deviation for **5** is only slightly larger. The same applies for **4** and **6**, where the C(2) to A–F average distance is somewhat smaller. The average A–F distances in the ketones are longer than in the enols, but since the distances themselves are long, they cannot be connected with the observed stability differences.

However, we note that the angles of the *o*-Me carbons with the mesityl rings are larger in **5** than in **2**. Whereas the larger angle for **2A** is C(12)C(13)C(18) (123.8 (5)°) and for **2B** C(12)C-(17)C(20) (124.0 (5)°) there are three angles wider than 125° for **5** (C(18)C(23)C(26) 125.5 (6)°, C(18)C(19)C(24) 126.4 (6)°, C(9)C(14)C(17) 126.2 (8)°). The latter values are larger than the corresponding values for trimesitylmethane (124.5°)[56] and they seem to indicate one of the ways by which **5** relieves the crowding between neighboring mesityl groups.

We conclude that **5** shows a larger deformation in bond and torsional angles than **2**. Since the requirement for deformation may reflect higher steric interactions, **5** may be regarded as more crowded, which explains its lower thermodynamic stability.

Conclusions

The conformations of the enols and the ketones in the solid state show the same features that were deduced in solution by spec-

troscopic methods. These include the propeller arrangement of the three rings, the hydrogen-bond dependence of the OH conformation in the enols, and the torsional ArCO angles in the ketones. The knowledge of the solid-state structure can assist in understanding the details of rotational processes in solution.

Experimental Section

Materials. Compounds **2-6** were prepared according to literature methods: compound **2** by the previously described[12] modification of Fuson's method,[16b] compound **3** by reaction of 9-anthryl magnesium bromide with dimesityl ketene,[12] compounds **4** and **6** by Fuson's method,[16a] and compound **5** according to a recent report.[1] The detailed synthesis of trimesitylethylene **7** by dehydration of 1,2,2-trimesitylethanol[1] will be described elsewhere.[18]

Crystals for the X-ray diffraction of **3-5** and **7** were obtained from ethanol, of **6** from diethyl ether, and of **2** from petroleum ether (60–80 °C).

Crystallographic Data. Intensity data were measured with Philips PW1100 four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The crystal structures were solved by MULTAN 77[57] and refined by SHELX.[58] The refinement of the various structures was carried out in separate blocks: non-hydrogen atoms in one and hydrogen atoms in the other, with anisotropic thermal parameters for the former and isotropic for the latter. The scattering factors for O and C were taken from Cromer and Mann[59] and for H from Stewart et al.[60]

Trimesitylethenol (**2**) ($C_{29}H_{34}$), triclinic, a = 15.621 (8) Å, b = 15.774 (8) Å, c = 11.468 (6) Å, α = 100.51 (2)°, β = 82.70 (2)°, γ = 119.68 (2)°, space group $P\bar{1}$, Z = 4, R = 0.075, R_w = 0.065 for 5675 reflections [$F_o > 1.5\sigma(F_o)$, w = 2.5103/$(\sigma^2(F)$].

2,2-Dimesityl-1-(9-anthryl)ethenol·EtOH (**3**) ($C_{34}H_{32}O \cdot C_2H_5OH$), monoclinic, a = 8.919 (4) Å, b = 27.185 (14) Å, c = 12.153 (6) Å, β = 93.77 (2)°, space group $P2_1/c$, Z = 4, R = 0.084, R_w = 0.073 for 2627 reflections [$F_o > 1.5\sigma(F_o)$, w = 1.6256/$(\sigma^2(F) + 0.003F^2)$].

1,2-Dimesityl-2-phenylethenol (**4**) ($C_{26}H_{28}O$), triclinic, a = 11.960 (6) Å, b = 12.311 (6) Å, c = 8.014 (4) Å, α = 109.09 (2)°, β = 97.53 (2)°, γ = 72.80 (2)°, space group $P\bar{1}$, Z = 2, R = 0.078, R_w = 0.076 for 2356 reflections [$F_o > 1.5\sigma(F_o)$, w = 1.8288/$(\sigma^2(F) + 0.005F^2)$].

Trimesitylethanone (**5**) ($C_{29}H_{34}O$), orthorhombic, a = 17.183 (9) Å, b = 8.413 (4) Å, c = 16.503 (8) Å, space group $Pca2_1$, Z = 4, R = 0.065, R_w = 0.065 (unit weights), for 1332 reflections [$F_o > 0.0$].

1,2-Dimesityl-2-phenylethanone (**6**) ($C_{26}H_{28}O$), orthorhombic, a = 22.927 (11) Å, b = 15.359 (8) Å, c = 11.664 (6) Å, space group $Pbca$, Z = 8, R = 0.093, R_w = 0.083 for 1948 reflections [$F_o > 1.5\sigma(F_o)$, w = 1.9001/$(\sigma^2(F) + 0.0003F^2)$].

Trimesitylethylene (**7**) ($C_{29}H_{34}$), triclinic, a = 15.367 (8) Å, b = 10.323 (5) Å, c = 8.288 (4) Å, α = 107.64 (3)°, β = 84.45 (3)°, γ = 109.09 (3)°, space group $P\bar{1}$, Z = 2, R = 0.077, R_w = 0.082 for 3644 reflections [$F_o > 0.0$, w = 0.4702/$(\sigma^2(F_o) + 0.0042F^2)$].

Supplementary Material Available: Tables S1–S6 giving the bond lengths, Tables S7–S12 giving the angles, Tables S13–S18 giving the atomic coordinates, Tables S19–S24 giving the structure factors, and Tables S25–S30 giving the anisotropic vibrational tensors for compounds **2-7**, respectively (140 pages). Ordering information is given on any current masthead page.

(56) Blount, J. F.; Mislow, K. *Tetrahedron Lett.* **1975**, 909.

(57) Main, P.; Woolfson, M. M.; Lessinger, L.; Germain, G.; Declercq, S.-P., MULTAN-77, A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Universities of York and Louvain, Belgium.

(58) Sheldrick, G. M., SHELX-76, Program for Crystal Structure Determination, Univeristy of Cambridge, 1976.

(59) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(60) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.