Representation of the Strain in 2,2-Dimesitylethenol and Its 1-Alkyl Derivatives[1]

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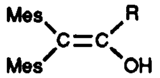
Received December 3, 1990

The strain present in 1-R-2,2-dimesitylethenols (R = H, Me, Et, i-Pr, t-Bu) is analyzed. The occupied volume (V^a) around a sphere centered on the mesityl *o*-methyl group closest to R is nearly linearly correlated with ΔG° values for the keto ⇌ enol equilibria, with ΔG^* values for rotation around the Mes—C═C bonds, with the torsional angle ϕ of the mesityl cis to R and with the bond angle R—C═C. On increase in the bulk of R the effective methyl radii calculated for the closest Me(β-ring)–Me(β'-ring) contact decrease below Charton's low value for the Me radius while the effective radii for the next to closest contact increase. The increase in the steric bulk is demonstrated by cuts through the "van der Waals body" of the molecule when R = H, t-Bu.

Steric effects dominate the chemical behavior of 2,2-dimesitylethenol (**1a**) and its derivatives **1b–e**.[2] These stable simple enols owe part of their thermodynamic and kinetic stabilities to the presence of the two bulky mesityl groups. The ΔG° for the keto ⇌ enol equilibria (a thermodynamic phenomenon),[2] the rotational barriers ΔG^* for the correlated two-ring flip around the Mes—C═C bonds (a kinetic phenomenon),[3] the Mes—C═C torsional angles, and the R—C═C bond angles (a structural phenomenon)[4,5] are linearly correlated among themselves and with Taft's E_s steric parameter of R. The association constants with a single DMSO molecule decrease with the increased bulk of R.[6]



Mes = mesityl

1a: R = H
b: R = Me
c: R = Et
d: R = i-Pr
e: R = t-Bu

Hence, it is interesting to apply other representations of the steric effect to this system. A graphical representation of the van der Waals body of the molecule, which was developed by one of us[7,8] recently, demonstrated the hindrance of approach of reagents to the double bond of 1,2-dimesityl-3-methylbuten-1-ol, which results in kinetic stability to ketonization.[9] Our success suggested a search for correlation between the "occupied volume parameter" in this approach and the E_s values or the other experimental parameters mentioned above.

Method and Terminology. We start by defining a measure of steric bulk, or crowdedness, at a point within the molecular domain. The point which constitutes the "anchor of measurement" is taken to be the center of a sphere (the "anchor sphere"). Spheres are demarked about all atoms in the molecule, at the appropriate van der Waals atomic radii. The union of these spheres is the "van der Waals molecular body". A portion of this body is circumscribed by the anchor sphere, and its volume V^a, the "volume enclosed by the anchor sphere", measures the steric bulk about the anchor. It is reasonable to place the anchor at one of the atoms of the molecule, or at several atoms successively. A reasonable radius for the anchor sphere is 3 Å. Smaller and larger radii are less discriminative because they contain too little or too much of the anchor environs, respectively. V^a values for typical neighborhoods were tabulated,[7] and the stature of V^a among other measures of steric bulk has been discussed.[7,8]

Table I. V^a Values for β-Mesityl Methyl Closest to R, ΔG° and $\Delta G^\ddagger$ Values (kcal mol^{-1}), and R—C═C and β-Mes—C═C Angles (deg) for Enols 1

R	V^a (Å^3 molecule^{-1})	$\Delta G^{\circ\,a}$ (hexane, 353.6 K)	$\Delta G^{\ddagger\,b}$	R—C═C bond angle^b	β-Mes—C═C torsional angle,^{c} ϕ
H	59.2	−2.12	14.2	118.1	50.2
Me	62.2	0.32	12.6	126.0	55.7
Et	63.2	0.83	11.95	127.4	58.3
i-Pr	66.4	0.90	11.7	127.7	60.1
t-Bu	67.2	3.63	10.4	133.2	63.7

^{a} Reference 2. ^{b} Reference 3. ^{c} Reference 4.

Application to Enols 1. To appraise the steric encumbrance in enols 1, we calculated V^a values at various atoms of these molecules. The most evident measure is the encumbrance about the methyl group closest to the substituent R (circled in Figure 1). The V^a values around these anchors were calculated from the crystallographic geometries for **1a–e**.[4] They are listed in Table I, together with the ΔG° (353.6 K, hexane)[2] values for the corresponding keto ⇌ enol equilibria, the ΔG^* for the two-ring flip process of the Mes_2C═ moiety, the torsional angles ϕ of the β-ring and the R—C═C bond angles. One may anticipate some geometric relaxation in solution, which would modify somewhat the V^a's. Plots of ΔG°, ΔG^*, and cos ϕ vs V^a (Figure 2) or a plot of the R—C═C bond angle vs V^a are nearly linear except for appreciable deviations of the isopropyl derivative **1d**.[10] They clearly demonstrate that both the extent of enolization and the rotational barrier decrease and the appropriate angles increase with the increased crowdedness imposed at the neighboring methyl group.

ΔG°, ΔG^*, and cos ϕ were also linearly correlated with Taft's steric parameter E_s.[2] The two approaches are

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[10] The reason for the large deviations in Figure 3 is not clear, although it may reflect different conformations of the i-Pr group in the solid state and in solution.

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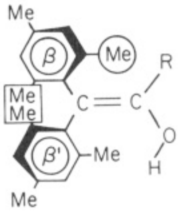

Figure 1. Designations of methyl groups in enols 1 for which interactions were calculated: methyl closest to substituent R circled, and "colliding" β- and β′-mesityl methyls enclosed in a square.

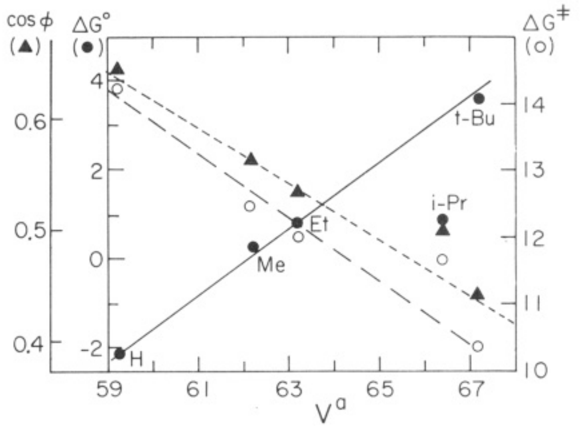

Figure 2. Plots of (i) $\Delta G°$ (kcal mol^{-1}, left-hand scale, ●) for the carbonyl–enol equilibria in hexane; (ii) $\Delta G^{\ddagger}$ (kcal mol^{-1}, right-hand scale, ○) for the correlated rotation of the mesityl rings in the Mes_2C= moiety; (iii) cos φ (deg, left-hand scale, ▲), the β-Mes—C=C torsional angle vs V^a (Å^3 molecule^{-1}). The points for i-Pr were excluded when drawing the slopes.

complementary in the sense that E_s measures the potential of a substituent R to inflict strain on its environment, whereas V^a measures the strain that has indeed been inflicted, manifested, e.g., by the higher cos φ and R—C=C angles for the bulkier R's. The approximate linearity of V^a with E_s indicate that the two factors apparently evolve in parallel in 1, and both affect the $\Delta G^{\ddagger}$ values by raising the ground state and contributing sterically to the rotational driving force. These results suggest that the skeleton is not sufficiently flexible to alleviate some of the strain that the substituent can and does bring in.

Why cannot the mesityl group of 1 rotate without an appreciable barrier so as to remove the methyl group circled in Figure 1 from a close contact with the substituent R? Inspection of space-filling models (which have the limitation that the bond lengths and angles are fixed) shows that this is mainly due to steric interaction between the methyl groups on the two rings during the rotation. This observation is corroborated when the distance between the Me(β-ring) and Me(β′-ring), which get into close contact, is calculated. For clarity, the close contact is enclosed in Figure 1 by a square, but since the Mes_2C moiety has a propeller conformation, there are two close contacts: between the methyl on the β-mesityl ring, and each one of the methyls on the β′-mesityl ring.

For **1a**, the two close $H_3C \cdots CH_3$ contacts are at 3.655 and 4.273 Å. When these numbers are halved, effective methyl radii at the contact of 1.83 and 2.14 Å, respectively, are obtained. These numbers come into perspective on recalling that the usually quoted van der Waals radius of CH_3 is 2.0 Å, that Charton's range for the methyl radius is 1.72–2.23 Å,[11,12] and that Sternhell's effective methyl radius is 1.80 Å.[13] Consequently, the closer of the close contacts is quite close, and even the other contact is still closer than the upper limit for a methyl radius. In other words, the circled *o*-Me⋯H(1) contact in **1a** brings the two squared mesityl methyls into a very tight contact.

Table II. Effective Methyl Radius (Å)^a at the Two Closer Methyl–Methyl Contacts

R	closest contact	next to closest contact
H	1.827	2.137
Me	1.782	2.241
Et	1.762	2.328
i-Pr	1.692	2.387
t-Bu	1.644	2.493

^{a} Half of the crystallographically observed distances.[4]

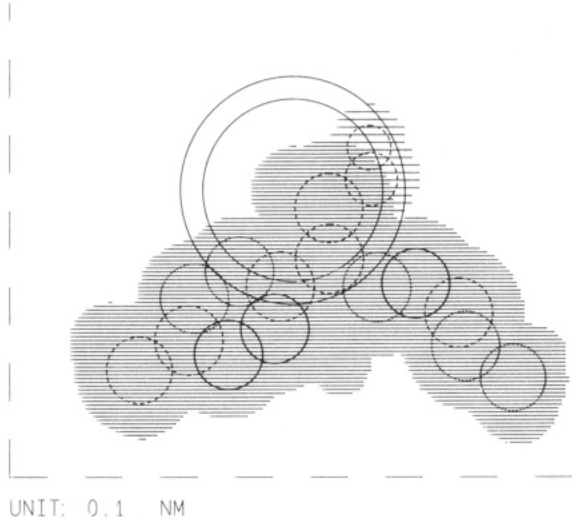

Figure 3. Cut through the van der Waals body of 2,2-dimesitylethenol **1a**.

The effective methyl radii, as derived from crystal geometries,[4] for the two close methyl–methyl contacts in **1a–e** (Table II) show that as R becomes bulkier, the strain at the closer contact increases, while that at the other close contact decreases. We are not aware of antecedents. This is not a computational result or a "theoretical prediction", since the numbers in Table II are simply half of the measured C⋯C distances.

Where are these numbers placed with respect to the range? The tightest close contact (1.644 Å for **1e**) is well below Charton's lower bound (1.72 Å)[11] whereas the least tight (2.493 Å for **1e**) is well above the upper bound (2.23 Å); the average of the closest sequence 1.827–1.644 Å is 1.74 Å, very close to the lower bound while the average of the other sequence 2.137–2.493 Å is 2.32 Å, very close to the upper bound. The average of all 10 numbers is 2.03 Å, virtually identical with Bondi's van der Waals radius of the methyl group.[14]

We thus conclude (a) that the molecules are inflexible because the substituent thrusts the methyls into the closest contacts conceivable, and (b) that the strain is partitioned among the two contacts in a way determined by the substituent R.

Finally, some of the points made above are demonstrated by cuts through the van der Waals bodies of the

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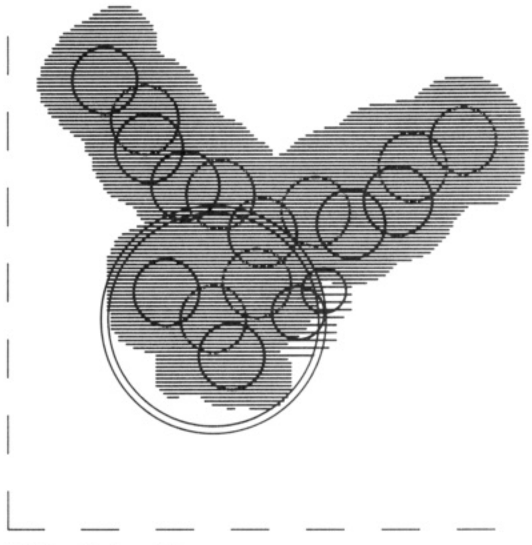

Figure 4. Cut through the van der Waals body of 1,1-dimesityl-3,3-dimethyl-1-buten-2-ol, **1e**.

least hindered α-H enol **1a** (Figure 3) and of the most hindered α-*t*-Bu enol **1e** (Figure 4). Hatching represents the section through the molecular body; sparse hatching pinpoints the hydroxyl group (up, right in Figure 3; bottom, right in Figure 4). In addition, circles indicate the position of carbons within 0.4 Å of the plane of cut. Hydrogens (apart from the hydroxylic) and other carbons are not marked. The plane of cut is parallel to the first inertial plane of the molecule, and passes through an assigned anchor atom. The external circle is the anchor sphere and to aid in visualization, the figures include an internal sphere, of radius r equal to the volume of a sphere of volume V^a (i.e. $r = 3V^a/4\pi)^{1/3}$). The more encumbered is the anchor, the narrower becomes the intercircle ring.

Notable features in Figures 3 and 4 are that the mesityl groups are locked into positions that are very far from coplanar and that the substituent affects the spatial relationship of the mesityls. In **1a** (Figure 3) the rings are at an appreciable angle whereas for **1e** (Figure 4) they are nearly parallel. In both cuts, the substituent head serves as anchor. In Figure 3, the anchor is H, V^a is quite small, 58.2 Å^3, and the ring between the circles is relatively wide. In Figure 4, the anchor is the tertiary carbon, the ring is thin, and V^a is enormous, 92.7 Å^3. This constitutes 82% of the conceivable maximum of 113.1 Å^3 for a sphere with a radius of 3 Å.

Acknowledgment. This work was partly supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to which we are grateful.

N^1,*N*^{5}-Bis(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienyl Radicals. An Electron Spin Resonance Study[1]

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Received November 9, 1990

A new class of nitrogen-centered free radicals, N^1,N^5-bis(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienyl radicals **1** have been generated by hydrogen atom abstraction from N^1,N^5-bis(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienes **2** or by photolysis of **2** or N^1,N^5,N^5-tris(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienes **3** using a UV or xenon lamp. Radicals **1** persist in solution and can be isolated as a diamagnetic dimer which, in solution, dissociates in part into **1** at room temperature. The thermodynamic parameters for the $\mathbf{4} \rightleftharpoons 2(\mathbf{1})$ equilibrium are 87.5 kJ mol^{-1} ($\Delta H°$) and 153 J K^{-1} mol^{-1} ($\Delta S°$), respectively. Radicals **1** have afforded the ESR spectra that show a_{N^1} (and a_{N^5}) 0.400–0.431, a_{N^3} 0.278–0.312, $a_{^{33}S}$ 0.48, and a_H (due to the protons of the arylthiyl groups) 0.022–0.076 mT. On the basis of these ESR results, it is concluded that in **1** the unpaired electron resides mainly on the three nitrogen and two sulfur atoms.

Recent interest in the chemistry of free radicals has been stimulated by the suggestion that polyradicals might be possible organic ferromagnets.[2] For the realization of such materials, the electron spins in the toporegulated π-networks of polyradicals should be appropriately arranged so as to induce ferromagnetic interactions among the spins. However, advances in this field have been seriously limited by the difficulties in the syntheses of such polyradicals because free radicals suitable for the syntheses of such polyradicals are rare.[3]

For the past 10 years, we have studied thioaminyl radicals ($R\dot{N}SR'$) and their analogues by ESR spectroscopy. In previous papers, we reported that some thioaminyls persist in solution for a long period, even in the presence of the atmospheric oxygen, and can be isolated as pure radical crystals[4,5] or diamagnetic dimers having a very low N–N bond strength.[6,7] As part of a program directed

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