the Taft–Pavelich equation

$$\log k = \rho^*\sigma^* + \delta_{E_S} + \log k_0 \qquad (4)$$

gives best results with separate lines for amides bearing groups with one or two α hydrogen atoms. It might be argued then that groups with no α hydrogens should lie on still another correlation line. It must be noted, however, that these authors find best results on correlation with the equation

$$\log k = \rho^*\sigma^* + \delta_{E_S}{}^c + h(n - 3) + \log k_0 \qquad (5)$$

and that while substituents with both one and two α hydrogens give an excellent fit to this equation, the *t*-Bu group deviates significantly. Bolton and Jackson have ascribed the effect of the *t*-Bu group to hyperconjugation. This is based on an analysis involving the $(n - 3)$ term in eq 5, which is considered to represent hyperconjugation by Hancock et al.[9] In our opinion this term represents an additional steric parameter, a point we shall take up in a future paper in this series.

It should be pointed out that our results for acid- and base-catalyzed ester hydrolysis,[1,2] our unpublished results for the reactions of aldehydes, acyl chlorides, and thioesters with hydroxide ion, water, and alcohols, and for the reaction of esters with ammonia show that the point for the *t*-Bu group lies on the correlation line. This leads us to the conclusion that the *t*-Bu group generally behaves normally in nucleophilic additions to the carbonyl group. Amide hydrolyses represent *an exception to this generalization.*

Supplementary Material Available. A table of ψ values for various reactions (1 page). Ordering information is given on any current masthead page.

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Sodium–Ethylenediamine Reductive Dimerization of Naphthalene to 5,6,7,12,13,14-Hexahydro-5,13:6,12-dimethanodibenzo[*a,f*]cyclodecene

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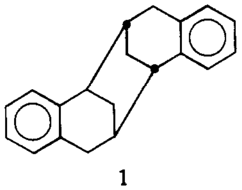
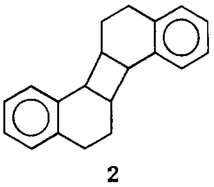
Crystallographic studies of the $C_{20}H_{20}$ reduced dimer, mp 179–180 °C, obtained from treatment of naphthalene with sodium and ethylenediamine showed the hydrocarbon to be the title compound. This analysis allowed ^1H NMR absorption assignments. Other properties of 1 and its oxidation products are reported.

The reaction of naphthalene or the dihydronaphthalenes with sodium and ethylenediamine[1a,b] affords a $C_{20}H_{20}$ reduced dimer, mp 179–180 °C, now shown by x-ray crystallographic analysis to have structure 1 rather than 2[1a,b] earlier proposed.



1



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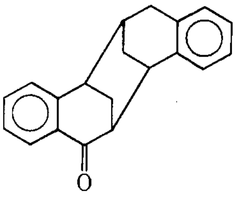

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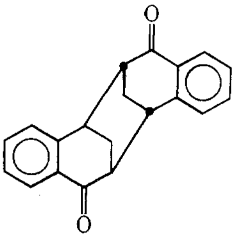


4

Dimer 1 is also formed by reaction of dihydronaphthalene with potassium *tert*-butoxide and dimethyl sulfoxide (Me_2SO).[2a] Wideman reported isolation of a crystalline 1,2-bisdialin, mp 179–180 °C, using the preceding reagents.[2b]

The crystal structure of the dibromo derivative of Heller's dimer, a nitrogen analogue of the title compound, has been determined[3a] and hydroxy ketone derivatives of the title compound have also been prepared.[3b] Otherwise structure **1** appears to be new.

We also report additional properties of 1 and its oxidation to the mono- and diketone, 3 and 4.

Results and Discussion

Figure 1 shows a stereoview[4a,b] of the dimer which consists of five six-membered carbon rings having a crystallographic center of symmetry.

Other data derived from the crystallographic study are summarized in Figures 2 and 3. Figure 2 shows the skeletal numbering[5] and carbon–carbon bond lengths[6] of 1. The bond angles as well as the torsion angles for the three unique ring systems of 1 are given in Figure 3. These torsional angles may be compared with those calculated for six-membered cycloalkanes.[7] Experimentally determined torsion angles for the cyclohexene ring agree best with torsion angles for the C_s barrier conformation calculated by Hendrickson.[7] Planarity of the benzene ring is indicated by torsion angles of approximately 0°. The bond angle formed by C(13)–C(14)–C(14a) shows a large distortion from the normal bond angle of 109.5° for a tetrahedral carbon atom. No other significant deviations from the expected bond distances and angles are observed.

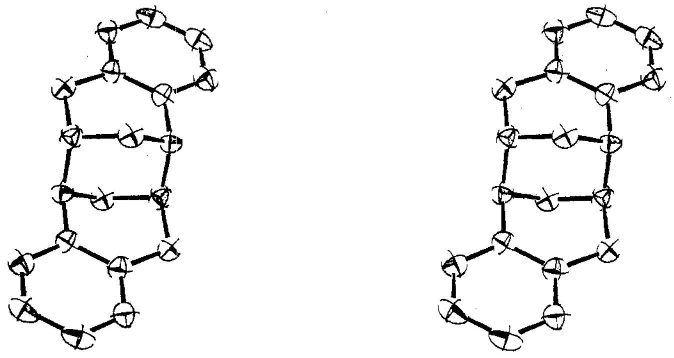


Figure 1. Stereoview of the carbon rings of 1.

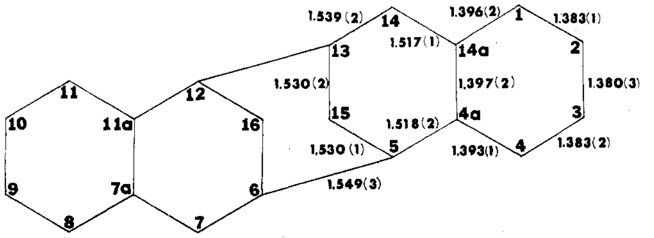


Figure 2. Carbon–carbon bond lengths and skeletal numbering for 1.

C–H bond distances range from 0.99(2) to 1.01(2) Å with an average value of 1.00(2) Å.

Our earlier assignment of structure 2 was based on the following evidence: (1) a strong ir band at 755 cm^{-1} suggesting four adjacent aromatic protons;[8a] (2) mass spectrum (70 eV) *m/e* (rel intensity) M$^+$ 260 (41), hemicleavage to *m/e* 130 (40), and 129 (100);[1b,8b,8c] (3) the presence of aromatic, benzylic, and aliphatic protons in the NMR spectrum in the ratio 8:6:6;[1b,8b] (4) GC retention time similar to other $C_{20}H_{20}$ dimers;[2a,8a,b] and (5) no obvious reaction on treatment with ozone or dilute bromine in carbon tetrachloride.[8a] More recently we have carried out pyrolysis studies of 1 which gave good yields of naphthalene, tetralin, and 1-methylindan in the ratio of 5.5:4.7:1.[8a] Attempts to dehydrogenate the hydrocarbon with Pd/C in refluxing 1-methylnaphthalene (bp 250 °C) or neat at 200 °C as well as 300 °C yielded unchanged 1. Oxidation of the hydrocarbon 1 with CrO_3 in acetic acid furnished a monoketone, **3**, mp 178–179.5 °C, and a diketone, **4**, mp 290–292 °C.[8a] The formation of only one monoketone and one diketone along with the high melting points and the poor solubility of 1 and the diketone were strong arguments for symmetry in the parent hydrocarbon 1 and the diketone **4**. Comparison of the ir and Raman spectra[8a,d] of the diketone 4 showed no correspondence of the major absorption bands. This suggested a symmetrical molecule lacking a dipole moment consistent with cis-anti-cis stereochemistry for the cyclobutane ring junction of 2. These observations agree, of course, with structure 1 as well.

Unfortunately, the diketone 4 is very insoluble and consequently of limited utility in NMR studies. Subsequently, we have applied base-catalyzed deuterium exchange to 4 and have attempted the preparation of its enol acetate and its benzylidene derivative. The diketone was unaffected by these procedures.

The foregoing evidence is most consistent with 5,6,7,12,13,14-hexahydro-5,13:6,12-dimethanodibenzo[*a,f*]cyclodecene-7,12-dione[5] as the structure of the diketone 4. The presence of the methano bridges in 4 explain its inertness to deuterium exchange and its failure to yield an enol acetate or benzylidene derivative.

We have also shown that the dimerization of dihydronaphthalene or the cyclization of 5 can proceed to 1 under nonreducing conditions.[2a,8a,b] For this reason, we favor anionic routes over a radical dimerization process.

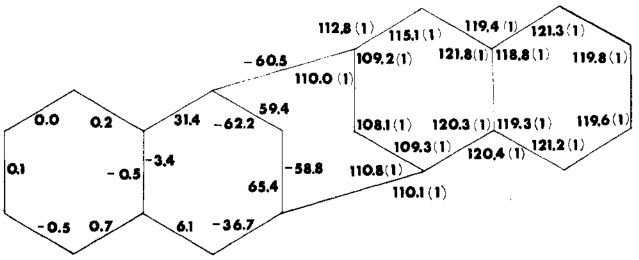
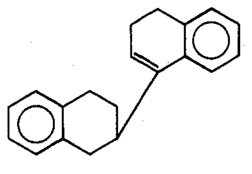
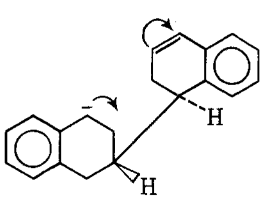


Figure 3. Bond and torsion angles for 1.

Structure 6 seems a likely intermediate to hydrocarbon 1 through the nucleophilic cyclization shown. A Dreiding model of 6 (anion assumed to be tetrahedral) shows that the conjugated double bond may be situated directly under the benzylic methylene group bearing the negative charge. This requires that 6 must have trans protons in order to cyclize to 1.

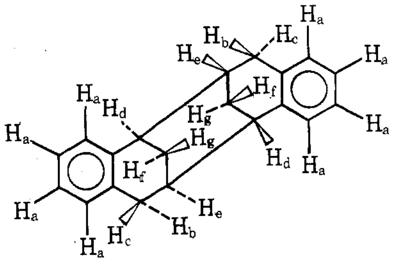


5



6

The rigorous crystallographic proof of structure for 1 allows conclusive assignment of peak absorption of its 100-MHz ^{1}H NMR spectrum. The rigidity of 1 provides a magnetically nonequivalent environment for geminal protons at C-7 and C-14 as well as C-15 and C-16 as shown for structure 7. Also, the centrosymmetry of 7 requires that each of these protons has an equivalent proton at the corresponding reflection position.[6] These are labeled accordingly.



7

The nonequivalent geminal protons couple to give $J_{H_bH_c}$ = 18 Hz and $J_{H_fH_g}$ = 13 Hz which is readily shown by irradiating the doublet corresponding to H_f or H_g and noting coalescence. The same is true for the signals of H_b and H_c with one further complication: H_b is represented by a doublet of doublets and coalesces to a doublet ($J_{H_bH_e}$ = 6 Hz) on irradiation of H_c. The absence of a measurable coupling constant between the vicinal protons H_c and H_e ($J_{H_cH_e}$ = 0 Hz) while noting one for H_b and H_e can be rationalized by calculating the dihedral angles between H_b and H_e (θ_1 = 36°) and H_c and H_e (θ_2 = 82°) and comparing the observed coupling constants to those predicted by the Karplus equation.[9] The dihedral angles were calculated from final coordinates (Tables I, II, and III) and the calculated coupling constants of $J_{H_bH_e}$ = 5.30 Hz and $J_{H_cH_e}$ = −0.11 Hz show good agreement with the observed values.

The choice of the remaining doublet ($J_{H_dH_e}$ = 1.5 Hz) for the signal of H_d is supported by coalescence to a singlet upon irradiation of the H_e multiplet. This is further supported by the presence of the same doublet (slightly shifted) in the

Table I. Positional Coordinates of All Carbon Atoms [a]

	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$
C(6)	6918 (2)	811 (2)	4952 (2)
C(7)	6702 (2)	−621 (2)	2834 (2)
C(7a)	4416 (2)	−1697 (2)	1231 (2)
C(8)	4067 (2)	−3153 (2)	−687 (2)
C(9)	2009 (2)	−4140 (2)	−2204 (2)
C(10)	256 (2)	−3698 (2)	−1824 (2)
C(11)	575 (2)	−2267 (2)	72 (2)
C(11a)	2639 (2)	−1257 (2)	1614 (2)
C(12)	2959 (2)	251 (2)	3711 (2)
C(16)	5015 (2)	1839 (2)	4698 (2)

[a] The atomic scattering factors for carbon were taken from "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 202. [b] The x, y, and z terms are expressed in fractions of the cell edges a, b, and c. Standard deviations for the last digit are in parentheses.

spectrum of the diketone 4 where H_d represents the only benzylic protons.

It is fortunate that H_b and H_c can be differentiated through their observed coupling constants with H_e. Such is not the case with H_f and H_g. Both parts of the doublets for H_f and H_g resemble broad unresolved triplets (5–8 Hz wide at peak half-height). Their shapes change to that of unresolved doublets on irradiation of H_e or H_d. It was noted that both H_e and H_d nearly halve the angle between H_f and H_g (all angles calculated to be 54–65°). The equal bond angles would explain why the splitting patterns of H_f and H_g are very similar and the magnitude of the bond angles could explain why the coupling constants may be small enough (calculated to be from 1.2 to 2.7 Hz) to be effectively hidden in the broad signals previously noted.

Experimental Section

Preparation of 5,6,7,12,13,14-Hexahydro-5,13:6,12-dimethanodibenzo[*a,f*]cyclodecene (1). The hydrocarbon dimer 1 was prepared by stirring 12.8 g of naphthalene, 10 g of sodium spheres, and 230 ml of anhydrous ethylenediamine at 50 °C for 2 h in a previously described stir-shredding device.[10] The reaction mixture was kept under a blanket of nitrogen. The product mixture was allowed to cool and was then cautiously poured onto crushed ice (1–2 kg). Aqueous HCl (2200 ml of 10%) was added and the resulting mixture was extracted with 2 × 500 ml of ether. The extract was washed with 50 ml of 10% HCl, then with water and finally dried ($MgSO_4$). Concentration and Kugelrohr distillation at 160–170 °C (0.1 mm) gave 4.2 g of a dimer fraction.

The above fraction was recrystallized from toluene to give 0.5 g of colorless 1: mp 179–180 °C; ir (KBr) prominent bands at 755, 741, and 712 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 260 (41), 131 (38), 130 (40), 129 (100), 128 (63), and 115 (21); ^1H NMR ($CDCl_3$) δ 7.25–6.97 (m, 8, ArH), 3.27 (d of d, $J_{H_bH_e} = 6$ and $J_{H_bH_c} = 18$ Hz, 2, $ArCH_2$), 2.87 (d, $J_{H_bH_c} = 18$ Hz, 2, $ArCH_2$), 2.85 (d, $J_{H_dH_e} = 1.5$ Hz, 2, ArCH), 2.21–1.94 (m, 2, $ArCH_2C\mathbf{H}$), 1.78 (d, $J_{H_fH_g} = 13$ Hz, 2, $ArCHC\mathbf{H}_2$), and 1.34 (d, $J_{H_fH_g} = 13$ Hz, 2, $ArCHC\mathbf{H}_2$); uv max (95% ethanol) 260 nm (log ϵ 2.97), 266 (3.16), and 273 (3.20).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.85.

Crystal Preparation and Measurement of Crystals. Crystals of 1, as clear needles suitable for data collection, were grown from a benzene–ethanol solution. Preliminary investigation of the data crystal on a Nonius CAD-4 automatic diffractometer indicated a triclinic space group. Least-squares cell dimensions were obtained from the averages of the $+2\theta$ and -2θ values of 20 pairs of reflections measured at ambient temperature (27 °C) using Cu Kα_1 radiation (λ = 1.5405 Å).

The 1162 intensity data, comprising all unique reflections with $2\theta \leq 130°$, were measured using Ni-filtered Cu K$\bar{\alpha}$ radiation (λ = 1.5418 Å) on a Nonius CAD-4 automatic diffractometer. The data were collected using θ–2θ scan technique in which the scan width was calculated as $1.0 + 0.1 \tan \theta$. The maximum scan time was 50 s with ⅔ of the time spent while scanning the peak and ⅙ on each the left and right background. A total of 122 reflections were considered indistinguishable from background, having a net count less than $1.4(T)^{1/2}$ (T = total count). These reflections were assigned intensities equal to $1.0\sqrt{T}$.

Crystallographic Structure Determination and Refinement. The overall temperature factor and scale were determined.[11] The normalized structure factors E were calculated, and a statistical test of their distribution strongly indicated a center of symmetry. The space group was thus determined to be $P\bar{1}$.

The structure was solved by direct methods using the program MULTAN.[12] The phases for 151 normalized structure factors greater than 1.5 were used in generating an E map. The E map calculated from one of several phase sets revealed the position of all ten carbon atoms contained in the asymmetric unit. The initial structure factor calculation gave an R [$= \Sigma||kF_o| - |F_c||/\Sigma|kF_o|$] of 0.40. After three cycles of least-squares refinement, all carbon atoms were given anisotropic temperature factors. Two subsequent cycles of refinement resulted in an R which converged at 0.12. Positions of the ten hydrogen atoms in the asymmetric unit were calculated on the basis of geometric considerations and compared with peaks appearing in the calculated difference Fourier. All ten hydrogens were thus located and included in the refinement with isotropic temperature factors. The refinement was terminated when all shifts were less than ½ of the corresponding standard deviation. A final difference Fourier map was calculated in which all electron densities were between −0.15 and 0.15 e $Å^{-3}$.

All least-squares refinements were carried out by the block-diagonal least-squares program of Ahmed.[13] The unweighted R based on the final parameters (Tables I, II, and II) was 0.044 for all data.[14] Each amplitude was assigned a weight based on a previously described[15] experimental weighting scheme. The quantity minimized in the refinement was $\Sigma w_F(|KF_o| - |F_c|)^2$. The average value of $W_F\Delta_F{}^2$ did not show significant variation with either $|F_o|$ or $\sin^2 \theta/\lambda$ in the structure factor analysis, validating the weighting scheme which was used.

The crystallographic data follow: $C_{20}H_{20}$; mol wt 260.18; space group $P\bar{1}$; $a = 6.9214 \mp 0.0004$ Å; $b = 7.5066 \mp 0.0008$ Å; $c = 7.9842 \mp 0.0005$ Å; $V = 340.74$ Å; $Z = 1$; F (000) = 140; $\alpha = 113.712° \mp 0.006°$; $\beta = 113.142° \mp 0.005°$; $\gamma = 91.523° \mp 0.006°$; $D_c = 1.268$ g/cm;^{3} and $D_m = 1.263$ g/cm^3 (measured by flotation in CCl_4/C_7H_{16} mixture).

Preparation of 5,6,7,12,13,14-Hexahydro-5,13:6,12-dimethanodibenzo[*a,f*]cyclodecene-7,14-dione (4). A sample (2 g, 0.008 mol) of 1 and 27.5 ml (30.3 g of solution, 0.03 mol) of a 10% aqueous chromium trioxide acetic acid solution[16] were stirred in glacial acetic acid (1 l.) for 10 days. The solution was poured into water whereupon a white solid separated. This was filtered out and recrystallized from toluene to give 1.5 g of colorless crystals, mp 288–291 °C. Concentration of the mother liquor gave an additional 0.3 g of crystals, mp 283–288 °C. The total yield was 81%.

Recrystallization of the first crop of crystals from toluene–2-propanol (1:1) gave 1.2 g of colorless 4: mp 290–292 °C; ^1H NMR ($CDCl_3$) δ 8.11 (d, J = 7 Hz, 2, peri ArH), 7.68–7.22 (m, 6, ArH), 3.35 (broad s, 2, ArCH), 2.71 (broad s, 2, ArCOCH), and 2.26–1.76 (m, 4, $ArCHC\mathbf{H}_2$); ir (KBr) prominent absorptions 1716, 1296, and 763 cm^{-1}; uv max (95% ethanol) 207 nm (log ϵ 4.70), 249 (4.48), and 295 (3.51); mass spectrum (70 eV) m/e (rel intensity) 288 (M^+, 71), 144 (100), 143 (43), 117 (1), 116 (1), and 115 (4).

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.46; H, 5.61.

Preparation of 5,6,7,12,13,14-Hexahydro-5,13:6,12-dimethanodibenzo[*a,f*]cyclodecen-7-one (3). Hydrocarbon 1 (504 mg, 0.002 mol) and 0.28 g (0.003 mol) of a 10% aqueous chromium trioxide–acetic acid solution[16] were stirred in glacial acetic acid (450 ml) for 9 h. The solution was poured into water (1.2 l.) and extracted with chloroform (450 ml). Gas chromatography of the concentrated extract showed a mixture of **1**:**3**:**4** (5.7:8.6:1.0).[17a] The components were separated by toluene elution through neutral alumina. Recrystallization from ether of combined fractions containing **3** gave 143 mg (0.0005 mol, 27%) of colorless needles: mp 176–178 °C (further recrystallization from ether improved the mp to 178–179.5 °C); NMR ($CDCl_3$) δ 8.09 (d, J = 7 Hz, 1, peri ArH), 7.62–6.96 (m, 7, ArH), 3.31 (d of d, J = 7 and 18 Hz, 1, ArC**H**), 3.14 (d, J = 4 Hz, 1, ArC**H**), 3.06 (d, J = 4 Hz, 1, ArC**H**), 2.91 (d, J = 18 Hz, 1, ArC**H**), 2.61 (broad s, 1, ArCOC**H**), 2.30–2.04 (m, 1, $ArCH_2C\mathbf{H}$), 1.96–1.63 (m, 3, ArCHC**H**), and 1.44 (d, J = 13 Hz, 1, ArCHC**H**); ir (KBr) 1670 (conjugated C═O) and 750 cm^{-1} (4 contiguous aromatic protons); uv max (95% ethanol) 253 nm (log ϵ 4.11), 274 (shoulder, 3.57), and 294 (broad, 3.29); mass spectrum (70 eV) m/e (rel intensity) M^+, 274 (32), 146 (90), 131 (21), 129 (100), 128 (25), and 115 (21).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.45; H, 6.58.

Attempted Catalytic Dehydrogenation of 1. A mixture of **1** (0.4 g), mp 177–179 °C, and 10% Pd/C (40 mg) was heated at 200–210 °C in a fused salt bath for 2 h. The reaction mixture was cooled, boiled with toluene (100 ml), and filtered to remove catalyst. The filtrate was rotary evaporated and pumped to dryness to give recovered **1**, mp 174–177 °C. The same sample was heated with new catalyst (40 mg) at 300 °C for 2 h and treated in the same manner to give 0.4 g of **1**, mp 169–175 °C, and mixed with starting material, mp 174–178 °C. GLC studies showed a single major peak with a trace of trailing impurity. Individual and mixed injections of starting material and sample showed identical retention times.[17b] A second sample of **1** (401 mg), catalyst (40 mg), and 1-methylnaphthalene (40 ml) were refluxed briskly for 2 h. The warm reaction mixture was filtered and washed with 90 ml of hot toluene. This solution was rotary evaporated and Kugelrohr distilled to remove toluene and 1-methylnaphthalene. The resulting tan solid was recrystallized from isohexane. The first crop yielded 345 mg, mp 177–179 °C (mixed with starting material, mp 176–179 °C); the second crop gave 28 mg, mp 175–177 °C, with a total return of 373 mg (93%) of recovered starting material. GLC studies of this sample showed results similar to those described above.

Acknowledgments. We thank the American Petroleum Institute for support during the early part of this work. We also thank the Continental Oil Co. for some current support, and the University of Oklahoma for providing computer time. We are grateful to Dr. P. W. Flanagan for his contribution in the early work.

Registry No.—**1**, 59434-72-9; **3**, 59434-73-0; **4**, 59434-74-1; naphthalene, 91-20-3; sodium, 7440-23-5; ethylenediamine, 107-15-3.

Supplementary Material Available. A listing of temperature factor parameters (Table II) and positional coordinates of hydrogen atoms (Table III) (2 pages). Ordering information is given on any current masthead page.

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(4) (a) To effectively utilize this stereoview, the reader should place the page on a table at normal reading distance, gaze past the structures, and rotate the page as needed until the figures merge. Alternatively, a stereoviewer can be used. (b) C. K. Johnson, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(5) We thank Drs. K. Loening and O. C. Dermer for advice on nomenclature.

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(14) See paragraph at end of paper regarding supplementary material. The structure factor table may be obtained directly from Dr. Dick van der Helm, Department of Chemistry, University of Oklahoma, Norman, Okla. 73069.

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Approach to the Conformational Analysis of Mannich Bases

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Conformational analysis of some Mannich bases and of the corresponding ammonium salts by NMR and CD indicates that in the solvents studied the hydrochlorides display a predominant conformation in which the two polar groups are gauche. In the case of the free bases, however, there is greater conformational freedom, the main factor in the equilibrium distribution of the conformers being the bulk of the substituents.

In a previous report on the stereochemistry of some α,β-disubstituted β-amino ketones[1] we observed that in solution the main factor in the distribution of the conformers at equilibrium is the bulk of the substituents, electrostatic interactions between the polar groups present in the molecule being of smaller importance. These last interactions are, on the other hand, very important in the case of the ammonium salts of the considered compounds, as other authors have demonstrated for analogous products of pharmacological and biological significance.[2]

Although there is abundant literature on the conformation of trisubstituted ethanes in solution (usually ethanes with halogens or alkyl groups),[3] no studies have been done on β-amino ketones with substituents in α or β position with respect to the carbonyl group. Continuing the studies on the reactivity and stereochemistry of Mannich bases, which are being carried out in our laboratories, in the present paper we report some aspects of NMR conformational analysis of 1-methyl- (Ia), 1-phenyl- (IIa), and 1-isopropyl-2-dimethylaminopropiophenone (IIIa) and their ammonium salts and of the NMR and CD studies of 3-methyl- (IVa) and 3-phenyl-4-dimethylaminobutan-2-one (Va), 3-phenyl- (VIa) and 3-methyl-4-piperidinobutan-2-one (VIIa), and of their hydrochlorides.

While derivatives I–III (R = C_6H_5) give easily analyzable NMR spectra, they do not allow a reliable CD conformational study owing to the presence of the conjugate aryl ketone chromophore, which makes problematic the use of the "octant rule".[4]