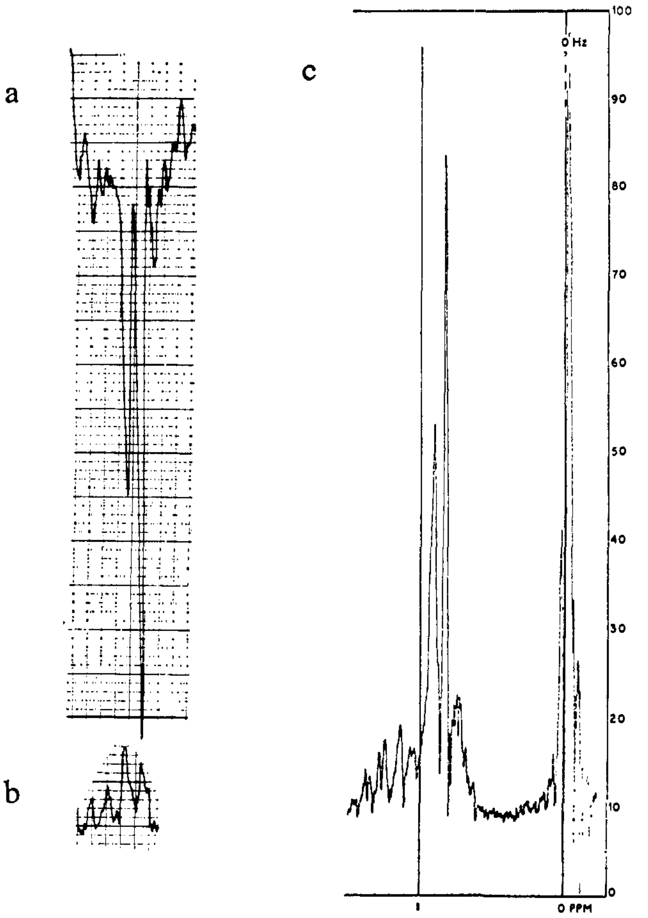

Figure 1. (a) Nmr spectrum of product mixture from a reaction of isopropyl chloride with sodium naphthalene carried out in a field of 60 G. (b) Same, after spin-lattice relaxation. (c) Reference spectrum of authentic propane in DME.

According to the radical-pair theory, T$_1$–S polarization is not a nuclear spin selection process. Instead, nuclear spin flips accompany T$_1$–S mixing, so that both the collapsed products and the escaped radicals from the set of *initial* engagements of alkyl radicals with naphthalene radical anions have nuclear spin polarization in the *same* direction. When the escaped radicals reengage naphthalene radical anions (not their former partners), one-fourth of the first collisions can be regarded as electronic singlets. Of these, a certain fraction collapses immediately (or during the first encounters of the reengagements) without undergoing additional nuclear spin flips. Thus, the polarization of the product formed in the set of initial engagements is reinforced, not suppressed.

It should be noted that T$_0$–S polarization can be effective in any field, so that low-field experiments would ordinarily lead to CIDNP reflecting both T$_0$–S and T$_1$–S contributions. In our case, the T$_0$–S contribution would be pure entropy polarization, while the T$_1$–S contribution would be pure energy polarization. Only energy polarization is evident (Figure 1). Thus, the T$_0$–S contribution to CIDNP appears to be suppressed for reactions carried out in low fields as well as in high fields. This extends to reaction fields near zero (earth's field), in which case no polarization is observed.

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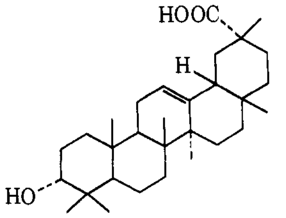
A Highly Twisted Carbon–Carbon Double Bond[1]

Sir:

In recent years compounds containing many types of strained double bonds have been prepared and studied, and particular interest has been given to rotation about a double bond, so called "torsional strain."[2] The high reactivity of such a system resulting from a decrease in the overlap of p electrons usually requires special synthetic methods be employed for their preparation.[3] We wish to report results related to preparation under acidic conditions of an unreactive highly torsionally strained double bond.

King and Morgan[4] reported that the triterpene katonic acid (**1**) underwent normal acetylation with acetic anhydride and pyridine but when treated with acetic anhydride containing a catalytic amount of perchloric acid it yielded a neutral keto acetate for which structure **2** was proposed. They noted that the uv max (EtOH) at 273 nm (ϵ 8900) was well outside the normal limits of 225–252 nm for α,β-unsaturated ketones.[5] This anomalous acetate also was reported to take up 2 mol of hydrogen to yield a product (uv max 217 nm (ϵ 5400, EtOH)) in which the keto group had been replaced by a methylene group. They also prepared, by lithium aluminum hydride reduction, a dihydro product with a uv max at 224 nm (ϵ 5200, EtOH). We have confirmed this latter result and also have obtained an isomeric dihydro alcohol (mp 169–173°) by lithium–ammonia reduction which has a uv max at 229 nm (ϵ 5180, EtOH).[6] These spectral properties, remarkable for compounds containing a lone carbon–carbon double bond, led us to undertake a crystal-structure analysis of this anomalous acetate.



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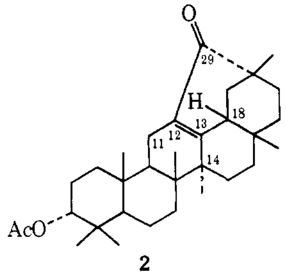

2

Crystals of the acetate, C$_{32}$H$_{48}$O$_3$, are monoclinic with the symmetry of space group $P2_1$; the unit cell con-

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[1] The crystal-structure analysis at Oak Ridge National Laboratory was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] For a general review of strained double bonds, see N. S. Zefirov and V. I. Sokolov, *Russ. Chem. Rev.*, 36, 87 (1967).

[3] J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970); J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970), and references cited therein.

[4] F. E. King and J. W. W. Morgan, *J. Chem. Soc.*, 4738 (1960).

[5] For a survey of ultraviolet spectra of unsaturated compounds, see A. I. Scott, "Interpretation of Ultraviolet Spectra of Natural Products," Macmillan, New York, N. Y., 1964.

[6] Both alcohols upon oxidation yielded the same enedione.

taining two molecules has parameters $a = 14.6934$ (8), $b = 12.7735$ (8), $c = 7.5595$ (3) Å, and $\cos\beta = -0.19662$ (5).[7] The structure was solved from 2183 X-ray reflections measured on the Oak Ridge computer-controlled diffractometer by a search of the Patterson function followed by tangent-formula phase refinement. It was assumed that the 16-carbon fragment containing C_1–C_{11}, C_{14}, and C_{23}–C_{26} has the configuration of the corresponding fragment in crystalline adiantol B bromoacetate.[8] The Patterson search procedure of Braun, Hornstra, and Leenhouts[9] yielded the orientation and position of the fragment in the unit cell; the corresponding atomic coordinates were used to calculate initial phase values for 218 selected[10] reflections. Tangent-formula refinement yielded phase values for all 416 reflections with normalized structure factor $|E| > 1.5$; the corresponding E map[11] displayed 34 of the 35 true carbon and oxygen positions among the 41 strongest peaks. The current value of the conventional discrepancy index $R(F)$ for all reflections is 0.04.

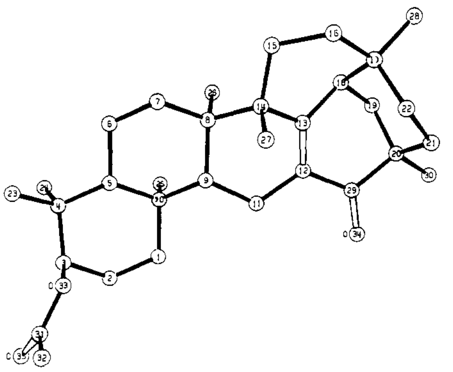


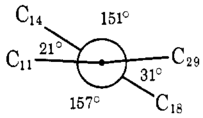
Figure 1. A perspective drawing of the molecule (excluding hydrogen atoms) viewed approximately along the b axis; the a axis is horizontal. Atoms linked by double bonds are connected by two lines.

Table I. Fractional Coordinates ($\times 10^4$) of the Carbon and Oxygen Atoms[a]

Atom	x	y	z	Atom	x	y	z
C_1	2480	5304	2798	C_{19}	6913	6033	8220
C_2	1480	5605	1979	C_{20}	7124	5676	6426
C_3	0792	4918	2652	C_{21}	7649	4616	6753
C_4	0915	4859	4716	C_{22}	7253	3786	7841
C_5	1947	4635	5533	C_{23}	0304	3953	5173
C_6	2171	4528	7593	C_{24}	0543	5891	5365
C_7	3126	4044	8268	C_{25}	2666	6508	5448
C_8	3910	4671	7683	C_{26}	4041	5703	8765
C_9	3642	4811	5582	C_{27}	4834	3084	6866
C_{10}	2683	5347	4872	C_{28}	7790	4422	11037
C_{11}	4431	5235	4683	C_{29}	6189	5577	5111
C_{12}	5385	5249	5866	C_{30}	7718	6471	5644
C_{13}	5546	4862	7540	C_{31}	0364	3580	0406
C_{14}	4870	4074	8049	C_{32}	0538	2481	−0094
C_{15}	5257	3727	10017	O_{33}	0883	3853	1984
C_{16}	6298	3410	10301	O_{34}	6128	5695	3487
C_{17}	6940	4188	9544	O_{35}	−0158	4188	−0495
C_{18}	6373	5180	8953				

[a] Estimated standard deviations of the atom coordinates lie between 0.003 and 0.008 Å.

The results of the crystal-structure analysis, presented in Figure 1 and Table I, show unequivocally that structure **2** is correct[12] and reveal the structural feature responsible for the large bathochromic shifts cited above. Closure of the sixth ring has forced the six carbon atoms associated with the double bond to depart from a common plane. The distortion is mostly but not entirely a torsion about the double bond; while atom C_{12} lies nearly in the C_{14}–C_{13}–C_{18} plane, atom C_{13} is 0.16 Å away from the C_{11}–C_{12}–C_{29} plane, corresponding to a slightly pyramidal configuration at C_{12}; the C_{11}–C_{12}–C_{29} plane makes an angle of 26° with the C_{14}–C_{13}–C_{18} plane. The overall geometry is most readily appreciated from the conformation angles about the $C_{12} \rightarrow C_{13}$ direction. It is interesting to note that the double bond length is 1.345 Å.



This distortion from coplanarity decreases the π-electron overlap from that normally present in a double bond and causes a mutual approach of the energy levels of the ground and excited electronic states, qualitatively accounting for the observed spectra.[13] The ORD curve for the LAH alcohol shows a large negative Cotton effect ($\Phi_{240}^{\mathrm{MeOH}} = -9500$); the sign follows the rules of Scott.[14] The ORD of the enone **2** in methanol also shows a negative Cotton effect; the molecular amplitude of rotation ($\Delta\Phi$) of 222,000 is the largest yet reported for this chromophore.[15] The unusual weakness of the Raman band at 1690 cm^{-1} assigned to the tetrasubstituted double bonds in the alcohols indicates a diminished polarizability ascribable to the reduced π-electron overlap.[16]

These materials do not display the high reactivity reported for simpler compounds containing strained carbon–carbon double bonds.[3,17] It is of particular interest that only the carbonyl group of enone **2** is reduced in a lithium–ammonia reaction. This observation and the lack of reactivity of all the compounds toward hydroxylic solvents indicate that addition reactions at the double bond offer no appreciable relief of strain in this complex ring system. Attempts to reverse the acylation reaction to yield the starting material, katonic acid, have not been successful; this most likely reflects the same lack of reactivity of the olefinic linkage.

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(7) The numbers in parentheses, corresponding to the least significant digits of the parameters, are estimated standard deviations from a least-squares analysis.

(8) H. Koyama and H. Nakai, *J. Chem. Soc. B*, 546 (1970).

(9) P. B. Braun, J. Hornstra, and J. I. Leenhouts, *Philips Res. Rep.*, 24, 85 (1969); see *Acta Crystallogr., Sect. B*, 26, 352 (1970), for an example of a structure solution by this method.

(10) J. Karle, *ibid., Sect. B*, 24, 182 (1968).

(11) J. Karle and I. L. Karle in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon, Oxford, 1965, Chapter 17.

(12) B. Tursch, J. Leclercq, and G. Chiurdoglu (*Tetrahedron Lett.*, 4161 (1965)) reported the preparation of a similar ketone from the triterpene mesembryanthenoidigenic acid, and, since their material was shown by nmr spectroscopy to contain one vinyl proton, they suggested that a reinvestigation of structure **2** was warranted. In view of the present results a study of their ketone would be interesting.

(13) For a complete discussion of spectral effects, see ref 2.

(14) A. I. Scott and A. D. Wrixon, *Tetrahedron*, 26, 3695 (1970).

(15) The authors are indebted to Dr. J. Fried and Dr. Lewis J. Throop of Syntex Research for measurement of the optical rotatory dispersions.

(16) The authors wish to thank Dr. J. R. Scherer of the U.S.D.A Western Regional Research Laboratory, Albany, Calif., for obtaining the Raman spectra.

(17) P. M. Lesko and R. B. Turner, *J. Amer. Chem. Soc.*, 90, 6888 (1968).

Of other examples of torsionally strained double bonds studied by the X-ray methods, a torsion angle of only 12° has been found for the 4,5-double bond in 3-methoxy-5β,19-cyclo-5,10-secoandrosta-1(10)-2,4-trien-17β-ol,[18a] and 8.6° for bicyclo[5.3.1]undec-7-en-11-one-1-carboxylic acid.[18b] The double bonds in the *trans*-cyclodecene–AgNO$_3$ complex[19] and the *trans*-cyclooctene–CuCl complex[20] are reported to be twisted about 40°. The small (~5 kcal) strain energy of *trans*-cyclodecene[19] when considered along with the recently observed rehybridization in olefin–transition metal complexes[21] suggests that this 40° angle of twist does not exist in the pure olefin hydrocarbon.

(18) (a) H. Hope and A. T. Christensen, *Acta Crystallogr., Sect. B*, 24, 375 (1968); (b) G. L. Buchanan, A. F. Cameron, and G. Jamieson, *Chem. Commun.*, 1145 (1969).

(19) P. Ganis and J. D. Dunitz, *Helv. Chim. Acta*, 50, 2379 (1967).

(20) P. Ganis, U. Lepore, and E. Martuscelli, *J. Phys. Chem.*, 74, 2439 (1970).

(21) L. Manojlović-Muir, K. W. Muir, and J. A. Ibers, *Disc. Faraday Soc.*, 47, 84 (1969).

(22) National Institutes of Health Postdoctoral Fellow, 1970–present.

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Equilibrium Constants for Gas-Phase Ionic Reactions. Accurate Determination of Relative Proton Affinities[1]

Sir:

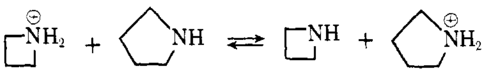
Experimental techniques presently used to measure thermochemical quantities such as heats of formation, bond strengths, proton affinities, and electron affinities have been limited to an accuracy seldom better than ±1 kcal/mol, yet more accurate values would be extremely useful for a wide variety of chemical problems. This communication describes the use of ion cyclotron resonance spectroscopy[2] for directly measuring equilibrium constants for proton-transfer reactions, permitting an accurate determination of relative proton affinities.

Most determinations of absolute proton affinities[3] have been by appearance potential methods and by an empirical correlation of excess kinetic energies in ionic reactions.[4] A qualitative method for the determination of relative proton affinities involves observation of the occurrence or nonoccurrence of ion–molecule reactions to place limits on proton affinities.[4,5] Combinations of these techniques can give proton affinities with an uncertainty of about 2–5 kcal/mol. These uncertainties arise from inaccurate heats of formation of neutrals and ions, problems with internally excited ions, and the inherently qualitative nature of the relative proton affinity limits. In contrast, the equilibrium technique described here suffers none of these difficulties and provides relative proton affinities accurate to better than ±0.2 kcal/mol.

The equilibrium constant for a proton-transfer reaction (1) is $K = [\mathrm{BH^+}][\mathrm{A}]/[\mathrm{AH^+}][\mathrm{B}]$. By measuring

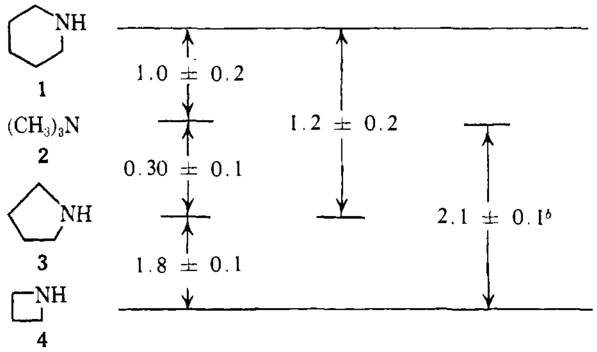
$$\mathrm{AH^+ + B \rightleftarrows BH^+ + A} \qquad (1)$$

the ratios $[\mathrm{BH^+}]/[\mathrm{AH^+}]$ and $[\mathrm{A}]/[\mathrm{B}]$ at equilibrium, the equilibrium constant and ΔG for reaction 1 can be calculated. The ΔG for proton-transfer reactions should be nearly equal to ΔH, giving the relative proton affinities of A and B,[6] hence $\Delta G \cong \Delta H = \mathrm{PA(A)} - \mathrm{PA(B)}$. Figure 1 illustrates an experiment in which a mixture of pyrrolidine, **3**, and azetidine, **4**, was introduced into a standard ion cyclotron resonance spectrometer[7] and the intensities of the azetidinium ions (*m/e* 58) and pyrrolidinium ions (*m/e* 72) were measured as the total pressure was raised. The ratio of their intensities becomes constant at about 1 × 10^{-4} Torr, indicating that equilibrium in the proton-transfer reaction 2 is established after about 30–50 collisions with $K = 22 \pm 2$ and $\Delta G^{25°} = -1.8 \pm 0.1$ kcal/mol. Double-resonance experiments were performed at high pressures and indicated that indeed reaction 2 proceeds in both directions. Similar experiments were performed on all systems reported here. Equilibrium data for mixtures of piperidine (**1**), trimethylamine (**2**), pyrrolidine (**3**), and azetidine (**4**) are presented in Chart I. The reproducibility obtained in several runs and the internal consistency of the over-



3 **4** (2)

Chart I. Changes in Free Energy, $\Delta G^{25°}$ (kcal/mol), for Proton Transfer Reactions such as Reaction 2[a]



[a] Piperidine (**1**) has the highest proton affinity in this series. [b] Determined by pulsed icr only because at high pressure the ions at *m/e* 58 and 60 were not resolved.

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(1) This work was supported by the National Science Foundation under Grant No. GP-15628 awarded to Michael T. Bowers, by the Petroleum Research Fund, administered by the American Chemical Society, under Grant No. 5031-AC4 awarded to Donald H. Aue, and by the National Science Foundation under Grant No. 4924, the National Aeronautics and Space Administration under Grant No. NGL-05-020-250, and the National Institutes of Health under Grant No. NIH GM 14725, which were awarded to John D. Baldeschwieler.

(2) For a description of the icr technique see J. D. Baldeschwieler, *Science*, **159**, 263 (1968); J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, 4, 114 (1971).

(3) The proton affinity of M, PA(M), is defined as the negative enthalpy change of the reaction $\mathrm{M + H^+ \rightarrow MH^+}$.

(4) See M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969), and references therein.

(5) V. L. Tal'roze and E. L. Frankevich *Dokl. Akad. Nauk SSSR*, 111, 376 (1956); J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1966; J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, 48, 1783 (1968); D. Holtz and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5913 (1969).

(6) Proton affinities are defined as enthalpies (ref 3), but for large molecules the ΔS for proton transfer should be negligible. Temperature-dependence studies are planned to verify this.

(7) M. T. Bowers and P. R. Kemper, *J. Amer. Chem. Soc.*, in press.