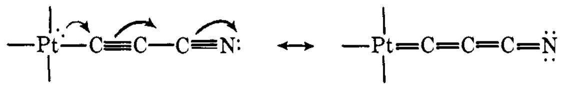
The intensity of 1742 independent nonzero reflections were taken with a Siemens four-circle diffractometer ($\theta \leq 45°$, Cu Kα radiation). Absorption corrections were computed with a program based on Busing and Levy's method.[7] The crystal structure was solved by three-dimensional Patterson–Fourier methods. The trial structure, with anisotropic vibrations and anomalous dispersion (real and imaginary) for platinum and phosphorus atoms, was refined by full-matrix least squares. All hydrogen atoms were assumed to be isotropic, and their parameters were excluded from refinement. During the refinement some anomalies were observed in the thermal parameters and in relatively low electron density distributions at C(4) and N(2) atoms. At the present stage of refinement the *R* index is 0.073. The geometry of the metal coordination is shown in Figure 1, and the most important bond lengths and angles with their estimated standard derivations are listed in Table I.

Table I. Interatomic Distances (Ångströms) and Angles (Degrees)[a]

Pt-P(1)	2.32 (1)	P(1)-Pt-P(2)	101.8 (0.3)
Pt-P(2)	2.33 (1)	P(1)-Pt-C(1)	90.5 (1.0)
Pt-C(1)	1.96 (3)	P(2)-Pt-C(2)	84.2 (0.9)
Pt-C(2)	2.02 (3)	C(1)-Pt-C(2)	83.5 (1.3)
C(1)-C(2)	2.65 (4)	Pt-C(1)-C(3)	172.2 (2.9)
C(1)-C(3)	1.24 (5)	Pt-C(2)-N(1)	169.8 (2.8)
C(2)-N(1)	1.17 (4)	C(1)-C(3)-C(4)	173.7 (3.7)
C(3)-C(4)	1.31 (5)	C(3)-C(4)-N(2)	168.5 (4.7)
C(4)-N(2)	1.16 (6)		

[a] Estimated standard deviations (in 10^{-2} Å) in parentheses.

The coordination around the platinum atom is strictly planar. Interesting features are the C(1)–C(3) distance of 1.24 Å, which is long for a "triple" bond, and the C(3)–C(4) distance of 1.31 Å, which is short for a "single" bond. These distances are also different from the corresponding distances in uncoordinated molecules of cyanoacetylene[8] and dicyanoacetylene,[9] and may indicate extensive electronic delocalization in the coordinated cyanoacetylido moiety, as can be envisaged in the valence-bond method by contributions from canonical form **4**.



$$\underset{\mathbf{3}}{-\mathrm{Pt}-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}\equiv\mathrm{N}:} \longleftrightarrow \underset{\mathbf{4}}{-\mathrm{Pt}=\mathrm{C}=\mathrm{C}=\mathrm{C}=\ddot{\mathrm{N}}}$$

3 **4**

Explicit in **4** is multiple bonding between platinum and C(1). Since it is reasonable to assume that multiple bonding exists between platinum and C(2), the similar Pt–C(1) and Pt–C(2) distances may imply a comparable π-acceptor capacity for the cyanoacetylido and cyano groups. Consistent with this idea of platinum–carbon multiple bonding are the platinum–phosphorus distances (2.32 and 2.33 Å), which are noticeably longer than Pt–P bonds in such compounds as $Pt(PPh_3)_2(CO_3)$[10] (mean 2.24 Å), $Pt(PPh_3)_2(O_2)$[11] (mean 2.27 Å), and $Pt(PPh_3)_2(NCCH{=}CHCN)$[12] (mean 2.28 Å).

Further photochemical studies of noble-metal complexes containing unsaturated organic ligands are being carried out.

Acknowledgments. This work was supported by a grant from the National Science Foundation, No. GP-10801.

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[8] A. A. Westenberg and E. B. Wilson, Jr., *J. Amer. Chem. Soc.*, 72, 199 (1950).

[9] R. B. Hannan and R. L. Collin, *Acta Crystallogr.*, 6, 350 (1953).

[10] F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *Chem. Commun.*, 408 (1967).

[11] T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *ibid.*, 743 (1969).

[12] C. Panattoni, R. Graziani, G. Bandoli, D. A. Clemente, and U. Belluco, *J. Chem. Soc. B*, 371 (1970).

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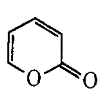
Received July 29, 1971

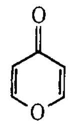
A Classification of 2- and 4-Pyrone as Nonaromatic on the Basis of Molecular Magnetic Susceptibility Anisotropies

Sir:

We wish to report the determination of the molecular magnetic susceptibility anisotropies of 2-pyrone (**1**) and 4-pyrone (**2**). The values obtained reveal a negligible out-of-plane net diamagnetic contribution due to nonlocal effects and suggest that these formally heteroaromatic compounds should be considered nonaromatic, at least by magnetic criteria.



1



2

The values of the magnetic susceptibility anisotropies, measured by microwave methods[1] in the gas phase, are: **1**, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 22.1 \pm 1.2$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 27.4 \pm 1.4$; **2**, $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 23.9 \pm 1.4$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 21.9 \pm 2.0$.[2]

The out-of-plane minus the average in-plane molecular magnetic susceptibilities, $\Delta\chi = \chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$, may be separated into local and nonlocal effects;

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[1] W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *J. Chem. Phys.*, 50, 1714 (1969). For the general analysis of an asymmetric top, see W. Hüttner and W. H. Flygare, *ibid.*, 50, 2863 (1969).

[2] The units are 10^{-6} erg/(G^2 mol). The *c* axis is the out-of-plane axis and the *a* axis contains the largest electric dipole moment in both molecules. The rotational spectrum of **1** gives rotational constants of $A = 5677.64 \pm 0.02$, $B = 2882.24 \pm 0.01$, and $C = 1912.13 \pm 0.01$ MHz. The rotational constants of **2**, provided by J. K. Tyler of the University of Glasgow, are $A = 5859.17 \pm 0.05$, $B = 2715.09 \pm 0.05$, and $C = 1855.55 \pm 0.05$ MHz.

the latter have significant values for aromatic[3] molecules.[4,5] The measured molecular magnetic susceptibility anisotropies of the 11 compounds listed in Table I[6] were used to determine the local group values of $\Delta\chi$,[4,5] listed in Table II. The calculated values ($\Delta\chi_{\text{local}}$) in Table I are the sums of the local group contributions and are shown to demonstrate the internal consistency of the fit.[7] On the other hand, the striking discrepancy between the $\Delta\chi_{\text{local}}$ and the $\Delta\chi_{\text{exptl}}$ for benzene and furan, the first two entries in Table III, indicate clearly the large nonlocal contribution ($\Delta\chi_{\text{nonlocal}}$) in these aromatic molecules usually attributed to significant π electron delocalization.[8,9] The agreement between the $\Delta\chi_{\text{exptl}}$ and $\Delta\chi_{\text{local}}$ for **1** and **2**, shown as the last two entries in Table III, reveals the absence of an appreciable contribution by $\Delta\chi_{\text{nonlocal}}$ in these molecules and leads to the suggestion that by magnetic criteria **1** and **2** should be classified as nonaromatic compounds.

Table I. $\Delta\chi$ Determined by Microwave Methods[a]

Molecule	$\Delta\chi_{\text{exptl}}$	$\Delta\chi_{\text{local}}$
Propene	-6.3 ± 0.4	-7.2 ± 1.6
Isoprene	-18.0 ± 1.1	-16.0 ± 2.4
Acrolein	-20.6 ± 1.2	-19.7 ± 1.9
Formaldehyde	-10.8 ± 0.4	-10.9 ± 1.1
Acetaldehyde	-8.9 ± 2.0	-9.3 ± 1.9
Dimethyl ether	$+4.6 \pm 0.5$	$+5.2 \pm 3.1$
Methyl formate	-7.0 ± 1.0	-7.3 ± 3.4
Vinylene carbonate	-14.5 ± 1.3	-15.7 ± 4.9
Maleic anhydride	-26.6 ± 1.8	-28.6 ± 4.5
2-Cyclopentenone	-19.0 ± 1.5	-16.5 ± 3.5
3-Cyclopentenone	-16.8 ± 1.0	-16.5 ± 3.5

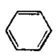
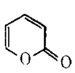
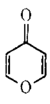
[a] Reference 6.

Table II. Local Group Contribution to $\Delta\chi$ for Organic Molecules

Group[a]	$\Delta\chi$ group
sp^3 carbon, $-\overset{\vert}{\underset{\vert}{C}}-$	$+1.6 \pm 0.8$
sp^2 carbon, $=C<$	-4.4 ± 0.4
Carbonyl oxygen, $=O$	-6.5 ± 0.7
Ether oxygen, -O-	$+2.0 \pm 1.5$

[a] The open valence can be bonded to other members of this group or to hydrogen which is assigned a $\Delta\chi$ of zero.

Table III. $\Delta\chi$ for Benzene, Furan, 2-Pyrone, and 4-Pyrone

Molecule	$\Delta\chi_{\text{exptl}}$	$\Delta\chi_{\text{local}}$	$\Delta\chi_{\text{nonlocal}}$
	-59.7[a]	-26.4 ± 2.4	-33.3 ± 2.4
	-38.7 ± 0.5[a]	-15.6 ± 3.1	-23.1 ± 3.6
	-24.8 ± 1.3	-26.5 ± 4.2	
	-22.9 ± 1.7	-26.5 ± 4.2	

[a] Reference 6.

Estimates of aromatic character by measurement of other properties indirectly related to $\Delta\chi$ have been reported. The difference between the measured molar magnetic susceptibility and that of a hypothetical localized[10] model is based on an average susceptibility[11] with corrections and uncertainties in the local values used to construct the model.[9] The recently suggested solvent-shift method[12] is derived in part from magnetic susceptibilities, but the effect is measured indirectly and the criterion requires a similar association constant between the solvents and acetonitrile. The ring current effect, which provides a model for one of the contributions to the chemical shift of aromatic protons,[4,9,13] has been extensively used to estimate magnetic susceptibility anisotropies. The difficulty of accounting for other contributions to chemical shifts when these are used to estimate ring currents is well recognized[9] and may explain the different estimates of this effect in **2**.[11,14] The microwave method uniquely gives a direct measurement of the molecular magnetic susceptibility anisotropies in isolated and unperturbed molecules.

Use of microwave-determined magnetic susceptibility anisotropies to assign aromatic character for cases where that issue is under question[15] appears, at present, to be preferable to the alternatives. The relationship of the magnetic criterion to thermodynamic and calculational criteria of aromatic character is not clear, although it is usually assumed that the different criteria will, at least qualitatively, follow the same trends.[9] In fact, quantitative correspondence between nmr estimates of ring current and resonance energy has been suggested[16] and criticized.[9,17] Relative thermodynamic stabilities favor a derivative of 2-pyrone over a derivative of 4-pyrone[15e] but evaluation of this result in terms of π bond energies is made uncertain

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[3] These molecules are defined as compounds containing $4n + 2\pi$ electrons in a cyclic conjugated system.

[4] R. C. Benson and W. H. Flygare, *J. Amer. Chem. Soc.*, **92**, 7523 (1970).

[5] R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **53**, 4470 (1971).

[6] See W. H. Flygare and R. C. Benson, *Mol. Phys.*, 20, 225 (1970), for a summary of previous work.

[7] These values differ slightly from the preliminary values[5] since strained compounds have been removed from the local model set.

[8] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, Chapter 4, provides an excellent review.

[9] A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968), has recently discussed magnetic susceptibility as a criterion of aromatic character in a critical review.

[10] H. J. Dauben, J. D. Wilson, and J. C. Laity, *J. Amer. Chem. Soc.*, **91**, 1991 (1969).

[11] A low molecular magnetic susceptibility has been reported for 2,6-dimethyl-4-pyrone by H. C. Smitherman and L. H. Ferguson, *Tetrahedron*, **24**, 923 (1968).

[12] F. A. L. Anet and G. E. Schenk, *J. Amer. Chem. Soc.*, **93**, 557 (1971).

[13] J. A. Pople, W. G. Schneider, and J. H. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

[14] C. T. Mathis and J. H. Goldstein, *Spectrochim. Acta*, 20, 871 (1964).

[15] The aromatic character of **1** and/or **2** has been discussed in a variety of ways: (a) A. R. Katritzky and J. M. Lagowski, "The Principles of Heterocyclic Chemistry," Methuen, London, 1967, pp 14, 30–32, 34, 50, 64, 167; (b) A. Albert, "Heterocyclic Chemistry," The Athlone Press, London, 1968, pp 336–342; (c) F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworths, London, 1963, pp 82–84; (d) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965, p 1024; (e) P. Beak, *Tetrahedron*, 20, 831 (1964); ref 11; ref 14.

[16] J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961), and subsequent papers.

[17] P. Beak, J. Bonham, and J. T. Lee, Jr., *J. Amer. Chem. Soc.*, 90, 1569 (1968).

by the unknown differences in σ bond energies of the isomers and intermolecular solvent associations.[17]

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Photochemistry of Olefins. Radical-Cation Behavior

Sir:

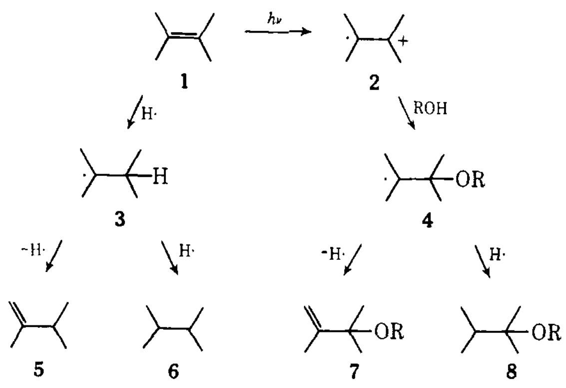
Recent studies in these laboratories and others have shown that either photosensitized or direct irradiation of medium-sized cycloalkenes in protic media results in light-induced protonation of the olefin followed by subsequent ground-state reactions of the resulting carbonium ion intermediate.[1-3] This process, which is thought to involve protonation of the highly strained trans isomer of the starting olefin,[1] is specific to six-, seven-, and eight-membered cyclic olefins and is not shared by acyclic, exocyclic, or smaller and larger ring cyclic olefins.[1]

We now wish to report a new photochemical process for olefins, involving direct irradiation, which occurs with both acyclic and cyclic olefins, regardless of ring size. It is illustrated by 2,3-dimethyl-2-butene (**1**), which on irradiation in alcoholic solvents readily affords principally a mixture of the ethers **7** and **8**,[4] accompanied by lesser amounts of the hydrocarbons **5** and **6** (see Table I). Similarly, in aqueous acetonitrile the corresponding alcohols **7** and **8** (R = H) are obtained. Analogous behavior is exhibited by the cyclic analogs 1,2-dimethylcyclopentene and -hexene.

Table I. Irradiation of 2,3-Dimethyl-2-butene (**1**)[a]

Solvent	Time, hr	Yield, %[b] **1**	**5**	6	**7**	**8**	9	**10**
H_2O, CH_3CN[c]	4	3	1.5	1	16	23	*d*	*d*
CH_3OH	4	6	4	16	30	37	*e*	*e*
CH_3OH[f]	128	42	1	2	2.5	3	*d*	*d*
C_2H_5OH	4	35	5	6	20	12	*e*	*e*
	8	3	5.5	6.5	23	16	*e*	*e*
n-C_4H_9OH	4	60	4	3	10	2	1	1
	16	5	7	7	23	10	4	4

[a] Unless otherwise indicated, irradiations were conducted with 3.40 g of **1** in 200 ml of solvent using a Hanovia Type L 450-W lamp and a water-cooled quartz immersion well. [b] Determined by gas-chromatographic analysis of aliquots removed from the reaction mixture relative to a saturated hydrocarbon internal standard. [c] 30% aqueous solution. [d] None detectable. [e] Trace. [f] A circular array of 16 G8T5 lamps, which emit principally at 253.7 nm, was used as the light source. The slowness of the reaction under these conditions is due in large part to the very small absorption by **1** at this wavelength.

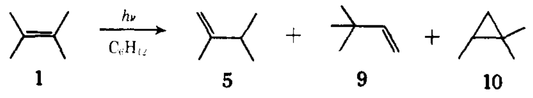


The formation of both saturated and unsaturated adducts suggests a mechanism involving the intermediacy of a radical cation of type **2** or, at least, a species exhibiting similar behavior, which undergoes nucleophilic trapping by the solvent to afford the alkoxy radical **4**. The hydrocarbon products **5** and **6** apparently arise *via* attack of H· on the starting olefin **1** as indicated. A principal source of H· appears to be from reaction of the ejected electron with solvent as shown in eq 1.[5] This is corroborated by the finding

$$e^- + CH_3OH \longrightarrow CH_3O^- + H\cdot \qquad (1)$$

that irradiation of **1** in methanol-*O-d* resulted in extensive incorporation of deuterium in products **5** and **6** but only minor incorporation in the ethers **7** and **8** (R = CH_3).

The radical-cation behavior is markedly sensitive to the degree of alkyl substitution. The trisubstituted analog 2-methyl-2-butene undergoes much slower reaction in methanol than does **1** under the same conditions and after 72 hr is only 80% converted, affording principally a mixture of hydrocarbons and ethers (yields of 42 and 9%, respectively). The radical-cation behavior is also markedly sensitive to the nature of the medium. This can be seen in Table I by the decrease in the rate of disappearance of **1** on going from water to 1-butanol. In aprotic media **1** undergoes instead a slow isomerization to a mixture of the isomers **5**, **9**, and **10**.[3] In 1-butanol, in which the rate of reaction *via* the radical-cation pathway is slow, appreciable amounts of the isomers **9** and **10** are formed in competition with the products **5**–**8**.



The conversion of **1** to photoproducts **5**–**8** is apparently a singlet-state reaction since attempts to induce reaction of **1** by triplet sensitization with *p*-xylene have been unsuccessful. It is not yet clear whether the radical-cation intermediate arises from direct photoionization of the olefin or whether it involves the singlet Rydberg excited state of the olefin. However, the ionization potential of **1** in hydroxylic media, which can be estimated from the Born equation to be about 2 eV lower than the gas-phase ionization potential of 8.30 eV,[6] is not sufficient to account for the fact that reaction can be effected at 253.7 nm (4.88 eV). On the other hand, the Rydberg excited state (λ_{max} 5.4 eV), although little studied,[7] has been assigned as the lowest lying

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(1) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **91**, 7466 (1969), and references cited therein.

(2) For a recent review, see J. A. Marshall, *Science*, **170**, 137 (1970).

(3) Unpublished results from these laboratories.

(4) Satisfactory analytical and spectral data have been obtained for all new compounds.

(5) A. Habersbergerova, Lj. Josimovic, and J. Teply, *Trans. Faraday Soc.*, **66**, 656, 669 (1970).

(6) J. P. Teegenand and A. D. Walsh, *ibid.*, 47, 1 (1951).

(7) To the best of our knowledge there is only one example in which photochemical behavior has been assigned to an olefin Rydberg state. This assignment, involving various gas-phase fragmentations, was made by default when it was found that the reactions occurred under conditions in which there was no concomitant cis-trans isomerization; see P. Borrell and F. C. James, *ibid.*, **62**, 2452 (1966); P. Borrell and P. Cashmore, *ibid.*, **65**, 2412 (1969).