formamide and subsequent treatment of the solution with hydrochloric acid. The white product gives the expected C, H, N, and Cl analyses and is a 2:1 electrolyte in water. The infrared spectrum (Figure 2) shows the strong, sharp OH frequency at 3370 cm^{-1}. It is possible to deuterate selectively the OH group by treatment of the complex with D_2O–DCl, thus confirming the OH assignment by the band shift to 2506 cm^{-1}. The ratio $\gamma_{OH}/\gamma_{OD} = 1.34$ is in good agreement with the theoretical value of 1.41.

Though $[Pt(etolen)_2]Cl_2$ is of low solubility in dimethylformamide, it is readily soluble as the tetraphenylborate salt in this solvent and reacts in the cold with the thionyl chloride–dimethylformamide reagent. The tetraphenylborate anion is decomposed in the reaction, and the white product crystallizes as the chloride salt whose infrared spectrum is shown in Figure 2 (dotted curve). The OH absorption at 3370 cm^{-1} has been removed, while new bands appear in the 700–800-cm^{-1} region.

No attempt has been made to separate the various isomers expected with these complexes. Nevertheless, the results serve to demonstrate that OH groups in neutral $[Co(NO_2)_3etoldien]$ and in positively charged $[Pt(etolen)_2]^{2+}$ are certainly capable of undergoing reaction.

J. A. Broomhead
Chemistry Department, School of General Studies
Australian National University, Canberra, A.C.T., Australia
Received May 23, 1968

A Cogwheel Effect in the Internal Rotations of Highly Hindered Systems

Sir:

Several recent references to hindered rotations in diarylcarbonium ions[1,2] prompts us to report the results of pmr studies in closely related systems. In particular, we are concerned with these properties of the dimesitylcarbonium ions and the respective substrates from which they can be generated in strong acid solutions (see Table I).

Table I. Pmr Data

Structure	Chemical shifts,[b] (Hz), of protons: *o*-Methyl	*p*-Methyl	Aromatic[f]	Methinyl	Temp, °C	References
$(Mes)_2CH^+$, **1**	7.80	7.70	3.09[a]	2.37	−52, −60, and +25	This work
$(Mes)_2COH^+$, **2**[b]	7.78	7.63	2.99		−52 and +25	This work
$MesC^+$, **3**[b]	7.62	7.72	3.08		−60 and +25	This work
$(C_6H_5)_2CH^+$, **4**			2.02[a]	0.19		*e*
$(C_6H_5)_2COH^+$, **5**			2.17			*e*
$MesCH^+CH_3$, **6**	±7.2 (doublet)	7.45	2.60	±1.30 (quartet)	−60	1
MesCOOH, **3a**	7.57[d]	7.71[d]	3.17		+40	This work
$(Mes)_2CHOH$, **1a**	7.87[d]	7.81[d]	3.35[d]	3.80[d]	+40	This work
$(Mes)_2C{=}O$, **2a**	7.81[d]	7.64[d]	3.10[d]		+40	This work
Mesitylene	7.75		3.22			*c*
Toluene	7.68					*c*

[a] The comparison of chemical shifts of the methinyl protons in **1** and **4** is only qualitatively valid since different media are used and bulk susceptibility corrections have not been made. [b] The carbonium ion species of the assigned structures were all generated in two solvents: concentrated sulfuric acid (45% or greater) and 10% CF_3COOH–90% $(CF_3CO)_2O$ solution (R. B. Moodie, T. M. Conner, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959)). The uv spectral and other characteristics by which these carbonium ions have heretofore been identified[3,4] were substantially the same in both media. These observations establish that the lowest temperature measurements (−60°) which could only be carried out in the CF_3COOH–$(CF_3CO)_2O$ solution were indeed taken on the carbonium ion and not on the trifluoroacetates. [c] Data from Varian catalog of nmr spectra taken in $CDCl_3$ solvent. [d] Data taken in CCl_4 at 40°. [e] D G. Farnum, *J. Am. Chem. Soc.*, **86**, 934 (1964). [f] *meta.*

The existence of ion **1** in sulfuric acid was first demonstrated by cryoscopic studies.[3] Its striking stability ($pK_{R^+} = -6.6$) was determined by means of uv spectral studies.[4] Deno and coworkers[4] have emphasized that the stability and spectral features of **1** cannot be understood on the basis of model examinations which reveal that the two mesityl rings are held rigidly at near right angles to each other, while their axes, and that of the (methinyl) hydrogen, join the cation center at 120° angles. However, the data given in Table I indicate that the models do not properly convey the rotational modes available both to dimesitylcarbonium ions or their respective tetracovalent precursors.

Pmr spectra of **1**, **2**, and **3** show sharp singlets for the methyl protons in both 60- and 100-Mc nmr measurements. The most distinctive features of these and other absorptions listed in Table I may be summarized as follows. (a) In **1**, **2**, and **3** the *o*-methyl protons are (all) magnetically equivalent and readily distinguished from the *p*-methyls. (b) In ions **1** and **2** (as well as the tetracovalent precursors) the *o*-methyls are more shielded than the *p*-methyls. (c) In the monomesitylcarbonium ions **3** and **6** the reverse is apparent: *i.e.*, the *p*-methyl protons are more shielded. (d) There is remarkably little difference in the chemical shifts (degree of shielding) of the *o*-methyl protons in all the mesitylcarbonium ions (**1**, **2**, and **3**), compared both to each other, to those of their precursors (**1a**, **2a**, and **3a**), or to the methyl-proton resonances in mesitylene and toluene. Moreover, the largest of these chemical shift differences (*ca.* 0.6 ppm between **1** and **6**) cannot be regarded as impressive. An entirely parallel situation prevails in a comparison among the corresponding *p*-methyl-proton resonances listed in Table I. (e) The (*meta*) aromatic protons in the mono- and dimesitylcarbonium ions **1**, **2**, and **3** are comparatively little deshielded in relation to those in the

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[1] G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *J. Am. Chem. Soc.*, **89**, 5259 (1967).

[2] R. van der Linde, J. W. Dornseiffen, J. R. Veenland, and Th. J. De Boer, *Tetrahedron Letters*, 525 (1968).

[3] M. S. Newman and N. Deno, *J. Am. Chem. Soc.*, 73, 3644 (1951).

[4] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); *J. Am. Chem. Soc.*, 77, 3049 (1955); H. A. Smith and B. B. Stewart, *ibid.*, 79, 3693 (1957).

precursor compounds, as well as the corresponding ring protons in mesitylene. The same protons in the monomesitylcarbonium ion **6** are somewhat more deshielded by its cationic charge but to a significantly lesser extent than those in the unmethylated diarylcarbonium ions **4** and **5**. (f) Finally, the methinyl proton at the carbonium ion center in **1** may be regarded as significantly deshielded in comparison to its chemical shift (value) in the tetracovalent precursor **1a** (τ 2.37 *vs.* 3.80); however, it is markedly less deshielded than in **6** and in the less stable[4] diphenylcarbonium ion (τ 0.19),[5] suggesting a much higher level of positive charge localized at this methinyl carbon in **4** and **6**.

Several novel conclusions may be drawn from these observations. For one, the magnetic equivalence of the *o*-methyl protons in all the dimesityl compounds examined, as well as their higher field positions relative to the *para* protons, suggests that the *o*-methyl groups are capable of ready exchange of their environments even at temperatures as low as $-60°$. At this temperature hindered rotation about the bond linking the carbonium ion center to the mesityl ring in **6** has been observed.[1] Nonetheless, relatively unrestricted internal rotations (about the same bond) in the dimesityl ions **1** and **2** and their precursors, which permit each of the *o*-methyl groups unhindered movement in and out of the shielding cone of the other ring, must be recognized in describing the motions of the two rings. Such rotational modes correlate both with the greater shielding of the two *o*- (*vs.* the *p*-) methyl groups as well as their magnetic equivalence.

An attractive possibility, on the basis of which we have undertaken feasibility computations, corresponds to intramolecular rotation involving the coordinated motion of the two mesityl rings. Herein it is assumed they both rotate with the same angular velocity about the bonds connecting them to the central carbon, and they are so arranged that, when one group lies in the plane formed by the central carbon and its bonds, the other is in a plane perpendicular to it. Internuclear distances between nonbonded atoms were calculated for a variety of conformations. Two types of hybridization (sp^3 and sp^2) of the central carbon atom and only normal values of the C–C and C–H bond lengths were considered. A single pair of methyls, one from each ring, was chosen, since the relative conformation of a methyl pair can be obtained from that of another pair by rotation through a suitable value of θ. The results of such calculations are the following: minimum carbon–carbon distances 3.39 Å at $\theta = 9°$ (sp^3) and 3.59 Å at $\theta = 0°$ (sp^2); minimum hydrogen–hydrogen distances 2.14 Å at $\theta = 18°$ (sp^3) and 2.37 Å at $\theta = 12°$ (sp^2).

Recalling the value of the van der Waals radius of hydrogen (1.2 Å) an overlap (encounter) during rotation (at 2.4 Å or less) could not be excluded for either the sp^3 or sp^2 case, though it would never be really severe for the latter. However, if further coordination in the rotation is assumed, the overlap clearly could disappear. Calculations were then performed in which both methyls were rotated 60° about the symmetry axis corresponding to the hydrogens' *getting out of each other's way without disturbing the carbon frame*. The results here show that when only one methyl is rotated, the hydrogen–hydrogen distances are more than adequate to allow full rotational clearance (2.64 and 2.83 Å at $\theta = 18°$ (sp^3) and 2.87 and 3.03 Å at $\theta = 12°$ (sp^2) depending on which methyl is rotated). If both are rotated, the departure from overlap is very much increased; consequently, the coordinated rotation of the mesityl rings is quite feasible and is assured, if some concomitant coordination in the internal rotation of a methyl group is permitted. For obvious reasons, we refer to these conditions which appear to satisfy the observed properties of the highly hindered system considered above as the "cogwheel effect." Further discussion of the other observations noted here for the dimesitylcarbinyl system is reserved for the occasion of a more definitive article in the near future.

Harold Kwart, Stanley Alekman
Department of Chemistry, University of Delaware
Newark, Delaware 19711
Received April 4, 1968

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(5) See footnote *e*, Table I.

Identification of Collision-Induced Fragmentation Pathways by Ion Cyclotron Double Resonance

Sir:

The utilization of mass spectrometry for the solution of several research problems has been based on the ability to predict, identify, and measure the degree of fragmentation of specific ions.[1,2] Detailed information regarding fragmentation processes at low pressure (10^{-8} torr) has come mainly from the study of series of compounds, including specifically labeled species, and by examination of metastable peaks. Intramolecular decompositions, induced by the collision of an ion with a neutral molecule, have not been extensively exploited for studying the nature of complex ions.[3,4] We now wish to describe a convenient technique, ion cyclotron double resonance,[5–7] for identifying collision-induced fragmentation pathways. This technique provides a useful method for exploring the character of specific ions.

At high pressures (10^{-5} torr) it becomes highly probable that ions collide with neutral molecules and that the equations of motion of related ions, such as parent and daughter ions (eq 1), are coupled.[8] Since ion–

$$\mathrm{M}\cdot^{+} + \text{neutral} \xrightarrow{k} [\mathrm{M} - \mathrm{A}]^{+} + \mathrm{A}\cdot + \text{neutral} \qquad (1)$$

molecule reaction rate constants are dependent on relative ion–molecule velocities, heating an ion with a radiofrequency electric field of the order of 0.05 V/cm will result in measurable changes in the concentrations

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(1) H. Budzikiewicz, C. Djerassi, and D. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967.

(2) W. Pike and F. McLafferty, *J. Am. Chem. Soc.*, **89**, 5953 (1967).

(3) C. Melton in "Mass Spectrometry of Organic Ions," F. McLafferty, Ed., Academic Press Inc., New York, N. Y., Chapter 2, reviews high-energy (>2 keV) collision-induced dissociations.

(4) F. Field, *Accounts Chem. Res.*, **1**, 42 (1968), discusses chemical ionization mass spectrometry where the ionization and fragmentation of a neutral substance are effected by reaction with an ionized reagent.

(5) L. Anders, J. Beauchamp, R. Dunbar, and J. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

(6) J. Beauchamp, L. Anders, and J. Baldeschwieler, *J. Am. Chem. Soc.*, **89**, 4569 (1967).

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(8) J. Beauchamp, *J. Chem. Phys.*, **46**, 1231 (1967); J. Beauchamp, Ph.D. Thesis, Harvard University, 1968.