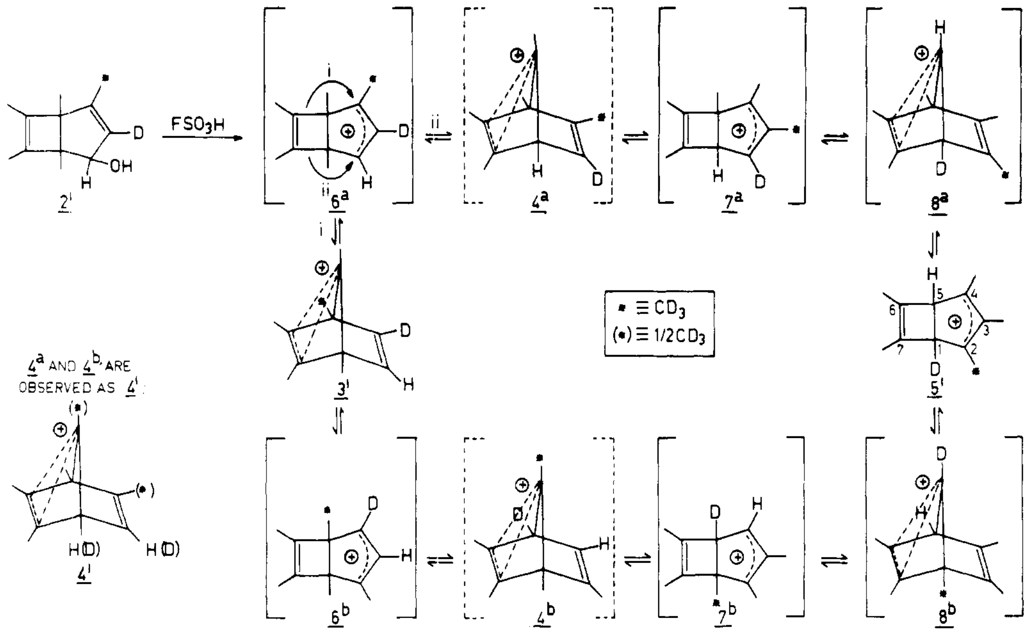

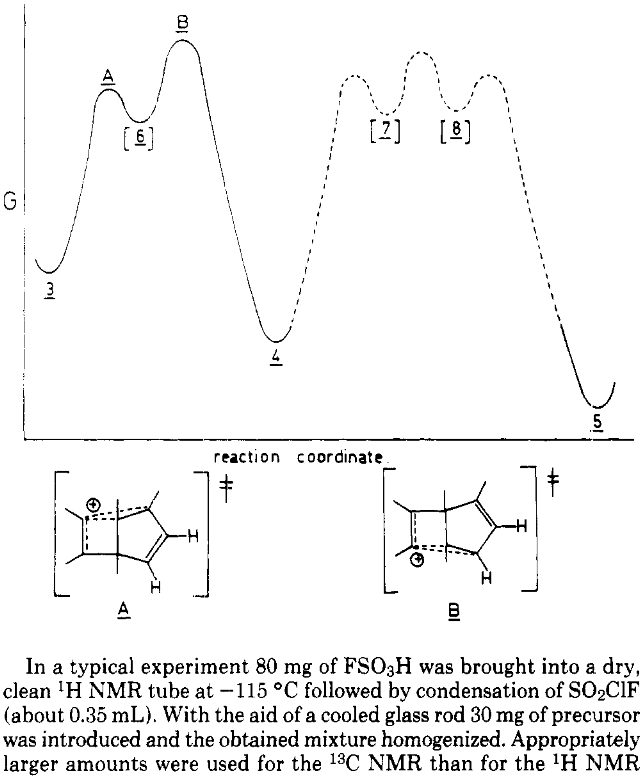

In a typical experiment 80 mg of FSO_3H was brought into a dry, clean ^1H NMR tube at −115 °C followed by condensation of SO_2ClF (about 0.35 mL). With the aid of a cooled glass rod 30 mg of precursor was introduced and the obtained mixture homogenized. Appropriately larger amounts were used for the ^{13}C NMR than for the ^1H NMR spectra.

1,2,5,6,7-Pentamethylbicyclo[3.2.0]hepta-2,6-dien-4-ol (2). To a stirred solution of 500 mg of ketone 1 in 25 mL of ether (freshly distilled from $LiAlH_4$), cooled to −10 °C, was slowly added 45 mg of $LiAlH_4$. This mixture was stirred for 1 h at −10 °C. After warming up to 0 °C a 20% NaOH solution and a 20% NH_4Cl solution were simultaneously added dropwise. After filtration the ether layer was washed with water untill neutral and dried ($CaCl_2$). The solvent was removed in vacuo using a rotary evaporator. The resulting white crystals were recrystallized from pentane (−30 °C) to give 381 mg (77%; one major stereoisomer) of **2**: IR 3320 cm^{-1} (broad); ^1H NMR (CCl_4) δ 5.00 (1 H, C-3, broad m), 4.07 (1 H, C-4, broad m), 1.65 (3 H, C-2 methyl, d, J = 1.5 Hz), 1.54 (6 H, C-6 and C-7 methyls), 1.08 and 0.93 (3 H each, C-1 and C-5 methyls), 1.01 (1 H, OH); mass spectrum parent peak m/e 178; correct elemental analysis.

1,5,6,7-Tetramethyl-2-trideuteriomethyl-3-deuteriobicyclo[3.2.0]hepta-2,6-dien-4-ol (2'). A solution containing 1 g of ketone 1 and 50 mg of CH_3ONa in 10 mL of CH_3OD was refluxed overnight. The methanol was evaporated under reduced pressure and the solid residue was treated with water and extracted with CH_2Cl_2. The organic layer was washed with water until neutral and dried over $MgSO_4$ and the solvent was removed in vacuo using a rotatory evaporator, giving a nearly quantitative yield of **1'**. Compound **1'** was treated with $LiAlH_4$ as described for ketone **1**, affording alcohol **2'**, whose ^1H NMR spectrum differed from that of **2** by lacking the hydrogen signal at δ 5.00 (due to hydrogen at C-3) and the allylic methyl signal at δ 1.65 (due to the C-2 methyl). Mass spectrum parent peak m/e 182.

Registry No.—**1**, 15971-77-4; **1'**, 61463-56-7; **2**, 61463-57-8; **2'**, 61463-58-9; **3**, 61505-78-0; **4**, 61505-77-9; **5**, 61463-63-6; CH_3OD, 1455-13-6.

References and Notes

(1) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **98**, 1551 (1976), and references cited therein.

(2) H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975), and references cited therein.

(3) H-N. Junker, W. Schäfer, and H. Niedenbrück, *Chem. Ber.*, **100**, 2508 (1967).

(4) For comparison with similar carbonium ions see N. C. Deno in "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., , 1970, p 796; D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, **91**, 261 (1972); R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2347 (1972); G. A. Olah and L. A. Paquette, *J. Org. Chem.*, **40**, 700 (1975).

(5) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2347 (1972).

(6) In ion **5** the CH_3 signal at δ 2.90 is observed as a doublet (J = 1.4 Hz). This is due to a coupling between the bridgehead hydrogen at C-1 (or C-5) and the CH_3 group at C-4 (or C-2), and not to a coupling between the hydrogen at C-1 (or C-5) and the CH_3 group at C-2 (or C-4). It is substantiated by the fact that in ion **5'** there is no such coupling.

(7) D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, **91**, 179 (1972).

(8) H. Hogeveen, C. F. Roobeek, and H. C. Volger, *Tetrahedron Lett.*, 221 (1972).

A Proposed Experimental Model for Molecular Orbital Calculations on Aryl Cations

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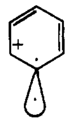
A proposal, made 15 years ago, that the phenyl cation may exist as the σ,π triplet diradical 1 in its ground state[1,2] has now been examined by several molecular orbital methods. Extended Hückel,[3] INDO (with and without geometry optimization),[4,5] CNDO/S–CI,[6] and ab initio[7,8,9] calculations all predict a ground *singlet* state for phenyl cation represented here, somewhat inadequately, with structure **2**.[10] CNDO/S–CI calculations on the singlet specie **3**, also proposed as a ground state alternative for phenyl cation,[2] predict that relative electronic state energies are **2** < **1** < **3**.[6]

The effect of substituents on the energy of singlet phenyl cation has been analyzed by extended Hückel[3] and ab initio[7a] methods, but the effect of substituents on the *relative* electronic energies of singlet and triplet phenyl cation has not received much study.[7b] INDO calculations on the 4-aminophenyl cation constrained to a symmetric benzene geometry have been reported.[4] While the symmetric INDO singlet **2** is *more* stable than the symmetric INDO triplet **1** by at least 3.5 eV,[11] the symmetric INDO singlet **4** is less stable than the symmetric INDO triplet **5** by 0.01 eV. Although the quantitative validity of these calculations may be questioned, the predicted substituent effect is reasonable. Stabilization of triplet phenyl cation, with its positive charge in the π system, by appropriately placed +R substituents is implicit in canonical structures such as **6** for the 4-aminophenyl cation.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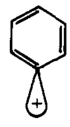
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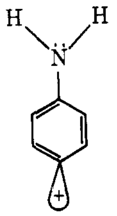
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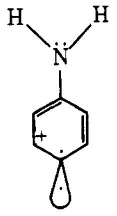
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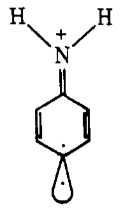
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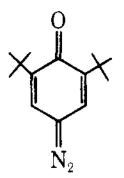
Multiplicities of the ground and low-lying excited states of the phenyl and 4-aminophenyl cations have not been experimentally determined, and it is, therefore, impossible to assess the validity of state multiplicity predictions made on those species by the various molecular orbital methods. Without an appropriate experimental model, the theoretical predictions are tenuous and of limited value. *It is the purpose of this note to point out that there is an available model; a substituted phenyl cation has been studied, and it has a triplet ground state.*

Pirkle and Koser investigated the photochemical decomposition of 3,5-di-*tert*-butylbenzene 1,4-diazooxide (**7**) in a variety of solvents including aromatic and aliphatic halides, benzene, cyclohexane, and a number of alkenes.[12–14] The reactive intermediate in those photolyses was regarded as the carbene, 3,5-di-*tert*-butyl-4-cyclohexadienonylidene. However, it may also be viewed as 3,5-di-*tert*-butyl-4-oxidophenyl cation (**8**), the oxido group of which is an outstanding +R substituent.[15] Other electronic states of **8** are represented by the carbenic structures **9**, the triplet which corresponds to **1**, and **10**, the singlet which corresponds to **3**. We suggest that this phenylium ion may be used as a model to test the reliability of molecular orbital calculations on aryl cations.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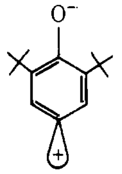
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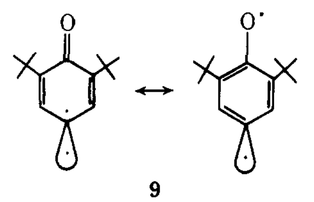
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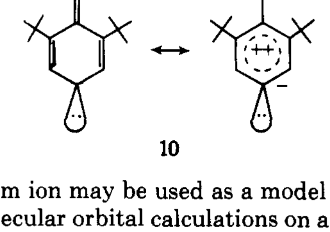
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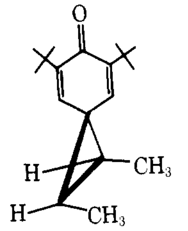
Pirkle and Koser found that the photolysis of **7** (λ >480 nm) in neat *cis*-2-butene gave the *cis*-spirooctadienone **11** with a high degree of stereoselectivity. When the olefin was diluted with hexafluorobenzene, the relative yield of the *trans*-spirooctadienone **12** increased, and it increased in proportion to the extent of dilution.[12,14] Skell's hypothesis[16] was applied to these data. It was reasoned that the singlet carbene **10** forms initially upon photolysis of **7** and adds stereospecifically to *cis*-2-butene to give **11**. Collision of **10** with the "inert" diluent hexafluorobenzene causes thermal deactivation of **10** to its triplet ground state **9** which then adds nonstereospecifically to *cis*-2-butene giving a mixture of **11** and **12**.[13,17,18] That the ground state is indeed a triplet was confirmed by direct observation.[17,18] When the *solid* diazo oxide **7** was photolyzed in an ESR probe at −180 °C, the spectrum of the triplet was recorded ($D = 0.3141$ cm^{-1}, $E = 0.0051$ cm^{-1}).[17]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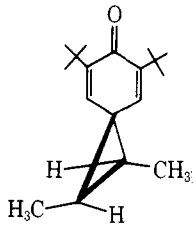
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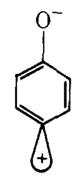
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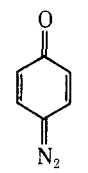
14

The state energy order for the 3,5-di-*tert*-butyl-4-oxidophenyl cation thus appears to be **9** < **10** < **8** and is, therefore, quite different from that predicted for phenyl cation. Here, then, is a test for the validity of any molecular orbital analysis of aryl cations. That is, if the calculations on phenyl cation, which predict a ground singlet state, are valid, similar calculations should predict a triplet ground state for the 3,5-di-*tert*-butyl-4-oxidophenyl cation.

Finally, we note that the olefin addition reactions of the 4-oxidophenyl cation (**13**) have not been studied nor has its ESR spectrum been observed even though benzene 1,4-diazooxide (**14**) is well known.[19] The *tert*-butyl groups in **7** are not innocuous; they impart solubility to **7** in nonpolar solvents, and they prevent the intermediate carbene (aryl cation) from reacting through its oxygen atom. However, it does not seem likely that attachment of *tert*-butyl groups to C-3 and C-5 in **13** would seriously alter *relative* electronic state energies, and computations on **13** would certainly be more economical than computations on **8**. Even so, the *tert*-butyl group perturbation needs to be determined.

Registry No.—**8**, 61446-34-2; **13**, 42766-45-0.

References and Notes

(1) R. W. Taft, *J. Am. Chem. Soc.*, **83**, 3350 (1961).
(2) R. A. Abramovitch and J. G. Saha, *Can. J. Chem.*, **43**, 3269 (1965).
(3) R. Gleiter, R. Hoffmann, and W. Stohrer, *Chem. Ber.*, **105**, 8 (1972).
(4) E. M. Evleth and P. M. Horowitz, *J. Am. Chem. Soc.*, **93**, 5636 (1971).
(5) C. G. Swain, J. E. Sheats, D. G. Gorenstein, and K. G. Habison, *J. Am. Chem. Soc.*, **97**, 791 (1975).
(6) H. H. Jaffé and G. F. Koser, *J. Org. Chem.*, **40**, 3082 (1975).
(7) (a) J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *Tetrahedron Lett.*, 2857 (1975); see ref 4b. (b) **Note Added in Proof.** After this paper was submitted, such a study did appear; see J. D. Dill, P. v. R. Schleyer, and J. A. Popel, *J. Am. Chem. Soc.*, **99**, 1 (1977).
(8) J. D. Dill, P. v. R. Schleyer, J. S. Binkley, R. Seeger, J. A. Pople, and E. Haselbach, *J. Am. Chem. Soc.*, **98**, 5428 (1976).
(9) Y. Apeloig, P. v. R. Schleyer, J. D. Dill, J. B. Collins, and J. A. Pople, Abstracts, 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1975, No. ORGN-1.
(10) The optimal geometry and charge distribution of singlet phenyl cation predicted by molecular orbital calculations are quite different from those depicted by structure **2**. See, for example, ref. 5 and 6.
(11) Calculations on the σ,π triplet were not performed. The INDO method generates the lowest energy triplet specie which, in this case, was predicted to be of the σ,σ type and to be 3.5 eV less stable than the ground singlet cation.
(12) G. F. Koser and W. H. Pirkle, *J. Org. Chem.*, **32**, 1992 (1967).
(13) W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 129 (1968).
(14) W. H. Pirkle and G. F. Koser, *J. Am. Chem. Soc.*, **90**, 3598 (1968).

(15) The transient species formed during the decomposition of other benzene 1,4-diazooxides have also been viewed as possible oxidophenyl cations. See, for example, (a) M. J. S. Dewar and K. Narayanaswami, *J. Am. Chem. Soc.*, **86**, 2422 (1964); (b) J. K. Stille, P. Cassidy, and L. Plummer, *ibid.*, **85**, 1318 (1963); (c) T. Kunitake and C. C. Price, *ibid.*, **85**, 761 (1963).
(16) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).
(17) G. F. Koser, Ph.D. Thesis, University of Illinois, Champaign-Urbana, 1968.
(18) See the footnote in ref 13.
(19) C. -H. Wang, *Proc. Chem. Soc., London*, 309 (1961).

Hypervalent Organoiodine. Reactions of Silver Arylsulfonates with Iodosobenzene Dichloride

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The synthesis of iodosobenzene diacetate (1) from iodosobenzene dichloride (2) and silver acetate, reported by Alcock and Waddington in 1963,[1] suggests that a similar synthesis of iodosobenzene ditosylate (3) should be possible. However, when we allowed 1 equiv of **2** to react with 2 equiv of silver tosylate in acetonitrile, compound **3** was not obtained. Instead, phenylhydroxytosyloxyiodine (**4a**, 46%) and *p*-toluenesulfonic acid (39%) were isolated, and silver chloride was obtained in only 62% yield. Compound **4a** was identified by its spectral (IR, NMR) comparison with authentic material prepared by the action of toluenesulfonic acid on **1**, a reaction described by Neiland and Karele in 1970.[2] That phenylhydroxytosyloxyiodine exhibits structure **4a** and not the tautomeric structure **5** has recently been established by x-ray analysis.[3] The simplest explanation for the formation of **4a** and toluenesulfonic acid in comparable yields rests on the assumption that ditosylate **3** enjoys intermediate existence. Hydrolysis of **3**, either by atmospheric moisture or by adventitious moisture in the reaction solvent, would lead to the observed products.

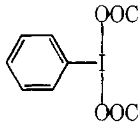
Indeed, when the reaction between **2** and silver tosylate was conducted under extremely dry conditions, compound 4a was *not* obtained. However, all attempts to isolate **3** failed. The crude product, a waxy, yellow solid, was resolved by trituration with ether into silver tosylate and a nearly colorless semisolid which rapidly changed to a black oil upon solvent removal. That the oil is an iodine-containing (not molecular I_2) compound was verified by elemental analysis, but a definitive structural assignment could not be made. When the oil was allowed to stand in air, it crystallized to a brown solid which was shown to consist *partially* of toluenesulfonic acid.

When **2** was allowed to react, in turn, with silver benzenesulfonate, silver *p*-chlorobenzenesulfonate, and silver *p*-nitrobenzenesulfonate, the hydroxysulfonates **4b** and **4c** and, presumably, the hydroxysulfonate **4d** were obtained (yields are given in Table I). Note that the yield of silver chloride failed to exceed 65% in all of those reactions. Compounds **4a–d** are insoluble in acetonitrile (the reaction solvent) and crystallize from solution subsequent to the removal of silver chloride. Crystallization may occur shortly after filtration or hours may pass before crystals appear. In the latter instance, addition of a small quantity (ca. 0.1 g) of water to the filtrate has been observed to facilitate product formation.

Authentic samples of **4b, 4c,** and **4d** were prepared by treatment of **1** with the appropriate sulfonic acid in acetonitrile and were characterized by elemental (C, H, I) and spectral analysis. The structures assigned to the materials derived from iodosobenzene dichloride (**2**) were then confirmed by spectral (IR, NMR) comparisons.

Table I

	$PhICl_2 + Ag^{+-}O_3SC_6H_4X$		$PhI(OAC)_2 + HO_3SC_6H_4X$	
X	Yield of 4, %	Yield of AgCl, %	X	Yield of 4, %
CH_3	46	62	CH_3	93
H	64	61	H	72
Cl	39	60	Cl	51
NO_2	32	47	NO_2	91



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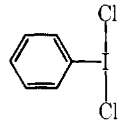

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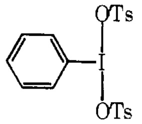

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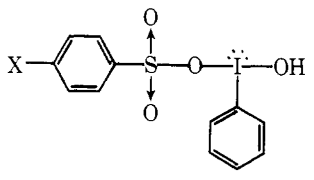

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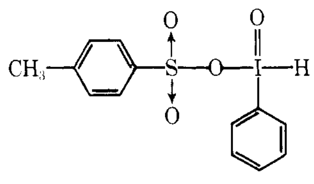
a, X = CH_3
b, X = H
c, X = Cl
d, X = NO_2



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Compound **4d** exhibited erratic behavior. For example, for three different $PhICl_2/AgO_3SC_6H_4NO_2$ runs, product melting points of 126–129, 141–143, and 153–156 °C were recorded. Similarly, for two different $PhI(OAc)_2/HO_3SC_6H_4NO_2$ runs, product melting points of 126–128.5 and 142–144.5 °C were observed, although most products derived from 1 melted in the 140–150 °C range. Melting points as high as 166–167.5 and 169–171.5 °C have been noted for "purified" **4d.** The NMR spectrum of **4d** in Me_2SO-d_6 has been difficult to reproduce. Two types of NMR spectra have been observed, and they exhibit significantly different aromatic patterns. One of these is nearly identical with the spectrum of a 1:1 mixture of iodobenzene and *p*-nitrobenzenesulfonic acid, and it seems that **4d** may undergo reductive decomposition in Me_2SO-d_6. We have been unable to isolate dimethylsulfone-d_6, the likely oxidation product, but if it is formed, it would be present in very small quantities. The NMR spectra of **4a, 4b,** and **4c** are clearly distinct from those of 1:1 mixtures of iodobenzene and the corresponding benzenesulfonic acids.

Finally, we have found that **4a** can be synthesized directly from iodobenzene. When a solution of iodobenzene (5 mmol) and silver tosylate (10 mmol) in acetonitrile was subjected to a stream of chlorine gas, **4a** was formed and was isolated in 48% yield.

Experimental Section

General. NMR spectra were recorded on a Varian Model A-60 NMR spectrometer, Me_4Si being used as an internal reference. IR spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer and were calibrated with polystyrene. However, reported band positions in the 8–24 μ range should be regarded as approximate