N. Greenlaw, M. A. Kelley, D. W. Potter, S. Rankowitz, and F. W. Stubblefield, *IEEE Trans. Nucl. Sci.*, **NS-23** (1), 398 (1976); (b) R. K. McMullan and, in part, L. C. Andrews, T. F. Koetzle, F. Reidinger, R. Thomas, and G. J. B. Williams (unpublished work), Brookhaven Neutron and X-ray Data Acquisition System. (c) Core and program limitations required the use of two blocks in the least-squares refinement.
(4) (a) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975); (b) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965); (c) B. G. Kusnetzov and P. A. Koz'min, *Zh. Strukt. Khim.*, **4**, 55 (1963).
(5) M. J. Bennett, W. A. G. Graham, J. K. Hoyano, and W. L. Hutcheon, *J. Am. Chem. Soc.*, **94**, 6232 (1972).
(6) We emphasize, however, that the term triple bond as applied to this compound is only a formalism. It has been pointed out that the assignment of a meaningful bond order in hydrogen-bridged species can be ambiguous, since metal–metal bonding is often intimately mixed with M–H–M bridge bonding.[5,7]
(7) M. R. Churchill and S. W. Y. Ni Chang, *Inorg. Chem.*, **13**, 2413 (1974).
(8) This is analogous to Bennett and Graham's description of the bonding in $H_2Re_2(CO)_8$,[5] which was pictured as a combination of (A) a direct Re–Re single bond, and (B) a four-center, two-electron H_2Re_2 overlap. In the case of the $H_8Re_2(PEt_2Ph)_4$, we would correspondingly have one of A and two of B.
(9) (a) J. Krausse, G. Marx, and G. Schödl, *J. Organometal. Chem.*, **21**, 159 (1970); (b) F. A. Cotton, J. M. Troup, T. R. Webb, D. H. Williamson, and G. Wilkinson, *J. Am. Chem. Soc.*, **96**, 3824 (1974).
(10) In $Li_4Cr_2(CH_3)_8 \cdot 4THF$ and $Li_4Mo_2(CH_3)_8 \cdot 4THF$, however, the Cr···$Li^+$···Cr and Mo···$Li^+$···Mo interactions occur at much longer distances [2.56 (3) in the Cr compound] and are clearly much weaker than the covalent Re–H–Re interactions observed in the present compound.
(11) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).
(12) (a) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973); (b) J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **96**, 6621 (1974); (c) R. Bau, B. Don, R. Greatrex, R. J. Haines, R. A. Love, and R. D. Wilson, *Inorg. Chem.*, **14**, 3021 (1975).
(13) D. W. Hart, T. F. Koetzle, and R. Bau, submitted for publication.
(14) R. D. Wilson, T. F. Koetzle, D. W. Hart, A. Kvick, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **99**, 1775 (1977).
(15) A. P. Ginsberg and M. J. Hawkes, *J. Am. Chem. Soc.*, **90**, 5930 (1968).
(16) C. White, A. J. Oliver, and P. M. Maitlis, *J. Chem. Soc. Dalton Trans.*, 1901 (1973).
(17) P. Dapporto, S. Midollini, and L. Sacconi, *Inorg. Chem.*, **14**, 1643 (1975).
(18) Neutron diffraction analysis of $[(Me_5C_5)Ir(H)_3Ir(C_5Me_5)]^+[BF_4]^-$ preliminary results: unit cell monoclinic, space group $P2_1/c$, $a = 10.423$, $b = 20.222$, $c = 11.174$ Å, $\beta = 108.35°$. The H atoms are essentially arranged in an equilateral triangle surrounding the metal–metal bond. Average distances and angles in the H_3Ir_2 core of the molecule are Ir–Ir = 2.455, Ir–H = 1.75, H···H = 2.14 Å, H–Ir–H = 75.8, Ir–H–Ir = 89.6°. R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, unpublished results (data collected at $T = 80$ K).
(19) The ^1H NMR spectrum was measured on a Varian XL-100 spectrometer operating at 100.1 MHz in the Fourier-transform mode, with benzene-d_6 as solvent (chemical shifts are reported relative to external TMS): τ 16.59 (quintet, $J_{P-H} = 9.28$ Hz, 8 H), 8.95 (d of t, $^3J_{P-H} = 15.17$ Hz, $J_{H-H} = 7.46$ Hz, 24 H), 8.12 (m, 16 H), 2.31 (m, 20 H). The four sets of resonances correspond to the hydridic, methyl, methylene, and phenyl hydrogen atoms respectively.
(20) Alfred P. Sloan Fellow, 1974–1976; NIH Research Career Development Awardee, 1975–1980.
(21) Recipient of the Walter C. Hamilton Memorial Scholarship, 1976.

Robert Bau,*[20] W. Eamon Carroll
Raymond G. Teller[21]
Department of Chemistry
University of Southern California
Los Angeles, California 90007

Thomas F. Koetzle*
Department of Chemistry
Brookhaven National Laboratory
Upton, New York 11973
Received March 1, 1977

Structure of $[Pt(en)(5'\text{-CMP})]_2 \cdot 2H_2O$. An Example of Direct Platinum–Phosphate Bonding

Sir:

The cross-linking of DNA by platinum has been suggested as a likely mechanism[1,2] for the anti-tumor activity of *cis*-$Pt(NH_3)_2Cl_2$, $Pt(en)Cl_2$, and related platinum complexes.[4,5] Covalent attachment of a platinum fragment to DNA could take place at a variety of sites on a double-stranded nucleic acid. In particular, there appears to be a distinct correlation between Pt-binding ability and the G + C content of a polynucleotide.[6] Although most investigators have favored the bases as the primary sites of Pt–DNA bonding, it has been suspected that the phosphate groups on the polynucleotide backbone may also play a part in stabilizing the Pt–DNA complex.[7] In this communication we report the existence of direct platinum–phosphate bonding in the structure of $[Pt(en)(5'\text{-CMP})]_2 \cdot 2H_2O$ (en = ethylenediamine; 5'-CMP = 5'-cytidine monophosphate).

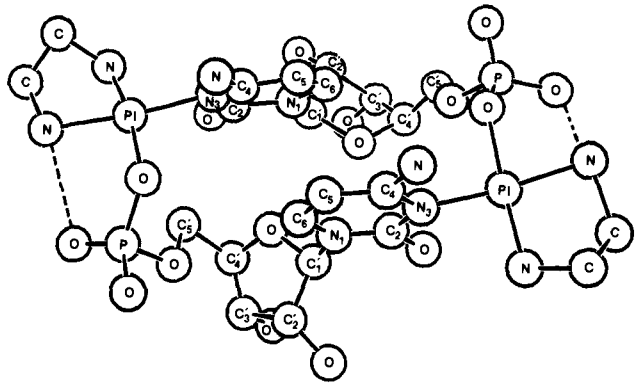
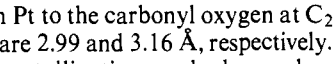


Figure 1. The molecular geometry of $[Pt(en)(5'\text{-CMP})]_2$.

$[Pt(en)(5'\text{-CMP})]_2$ was prepared by treating a solution of $Pt(en)Cl_2$ with 2 mol of $AgNO_3$,[8,9] filtering off silver chloride, and adding an equivalent amount of $Na_2(5'\text{-CMP})$. After the mixture (pH 6–7) was allowed to stand at room temperature for ~2 weeks, it was passed through Sephadex G-10 to separate the product from low molecular weight species such as unreacted starting material. Vapor diffusion of the resulting solution against methanol produces tiny prismatic crystals of the product. Crystals of $[Pt(en)(5'\text{-CMP})]_2 \cdot 2H_2O$ are monoclinic (space group $P2_1$), with $a = 15.059$ (9), $b = 11.674$ (7), $c = 12.353$ (21) Å, $\beta = 94.23$ (9)°, $Z = 2$. Data were collected on a Nonius CAD-3 automated diffractometer with Mo Kα radiation up to a 2θ limit of 45°. The structure was solved by heavy atom methods and refined to an R factor of 9.0% for 1200 nonzero reflections.[10,11]

The molecular plot of the dimeric molecule is shown in Figure 1. The CMP ligands are linked in a head-to-tail fashion by two bridging Pt(en) fragments, such that each Pt atom is bonded to the N_3 atom of one nucleotide and to a phosphate oxygen of the other. The cytosine rings within each dimer are positioned somewhat parallel to each other (angle between planes = 16°) at a distance of 3.51 Å apart. Average distances and angles in the molecule are as follows: Pt–O = 1.97, Pt–N_3 = 2.06; Pt–N(en) = 1.97 Å; O–Pt–N_3 = 90.4, N_3–Pt–N(en) = 95.6 and 174.7; O–Pt–N(en) = 88.2 and 174.2, N(en)–Pt–N(en) = 86.0°. The ribose sugar rings are in the C_2'-endo configuration, and the conformations about the glycosidic bonds are anti.[12] A strong hydrogen bond is found between a phosphate oxygen and an ethylenediamine nitrogen at a distance of 2.75 Å, so that in effect each phosphate group forms a hydrogen-bonded chelate about platinum:



Distances from Pt to the carbonyl oxygen at C_2 and the amino nitrogen at C_4 are 2.99 and 3.16 Å, respectively. The two water molecules of crystallization are hydrogen bonded to a phosphate group and to a carbonyl oxygen of one of the CMP ligands.

The structure of $[Pt(en)(5'\text{-CMP})]_2$ described here represents the first example of a platinum–CMP complex isolated and structurally characterized.[13] Platinum–phosphate bonding had not been previously found in a platinum nucleotide com-

plex, even though it had been demonstrated to exist in an inorganic pyrophosphate complex, $Pt_2(NH_3)_4(P_2O_7)$.[14]

Platinum-DNA binding through the backbone phosphate groups was first suggested by Morris and Gale in 1973,[7] who included such a model among a number of postulated modes of Pt-DNA attachment. Robins had earlier strongly implicated the importance of Pt-phosphate interactions by noting that the rate of formation of Pt-nucleoside complexes was considerably enhanced by the presence of phosphate groups on the nucleosides.[15] Additionally, Horacek and Drobnik found that the affinity of *cis*-$Pt(NH_3)_2Cl_2$ for DNA was markedly lowered in the presence of PO_4^{-}, implying that inorganic phosphate was competing with DNA for available Pt coordination sites.[16]

The structure of $[Pt(en)(5'\text{-CMP})]_2$ is consistent with those of other metal-CMP complexes. In $[Co(5'\text{-CMP})(H_2O)]_n$,[17] and in two different crystalline modifications of $[Cd(5'\text{-CMP})(H_2O)]_n$,[17,18] the CMP acts as a bridging ligand, with N_3 attached to one metal and the phosphate group to others. This same feature is seen in $[Pt(en)(5'\text{-CMP})]_2$, the main difference being that the Pt complex is not polymeric like the others. The simultaneous N_3-phosphate attachment which appears to be a recurring theme in metal-CMP complexes may indicate that the N_3 position of cytidine is not so strong a binding site as the N_7 position of guanosine or inosine,[19-22] and needs to be reinforced by additional phosphate-metal bonding. In $[Pt(en)(5'\text{-CMP})]_2$, the dimeric nature of the molecule, and the concomitant base/base stacking, may provide further stabilization for the structure.

Our results on $[Pt(en)(5'\text{-CMP})]_2$ do not imply that platinum-phosphate bonding is necessarily a feature of Pt-DNA interaction, but it does suggest that such bonding should be taken into account when models of Pt-DNA binding are formulated. The significance of the Pt-N_3 coordination is an interesting question. The N_3 position of cytosine is normally tied up by G-C base pairing in the double helix and is not available for complexation. It is conceivable, however, that during strand separation this position might become exposed and be attacked by platinum. The ethylenediamine-phosphate hydrogen-bonding found here (dotted lines in the figure) reinforces the point, made in our earlier paper,[19] that hydrogen bonding involving the amine ligands may be a stabilizing factor in Pt-DNA binding.

By now tentative conclusions about platinum binding to nucleosides and nucleotides are becoming available. There seems to be general agreement that strong binding takes place with guanine, and moderate binding with adenine and cytosine derivatives. Uracil, thymine, and their derivatives appear not to bind to Pt, except for the mysterious platinum uracil blues.[23] Recent structure determinations of $[Pt(en)(guanosine)_2]^{2+}$,[19] *cis*-$[Pt(NH_3)_2(guanosine)_2]^{2+}$,[20] *cis*-$[Pt(NH_3)_2(5'\text{-IMP})_2]^{2-}$,[21] and $[Pt(en)(5'\text{-IMP})_2]^{2-}$ [22] have shown that primary attachment of guanosine and the related inosine derivatives to platinum occurs at the nucleophilic N_7 position of the purine ring. With adenine, both N_7 and N_1 complexation has been found.[24]

For cytosine, N_3 has always been considered the most probable site for Pt complexation, although there have been earlier reports suggesting the 4-NH_2 group as an alternative possibility. The weight of available crystallographic evidence on a substantial number of metal-cytosine and metal-CMP structures now strongly supports N_3 as the dominant site of interaction.[17,18,25,26] Often metal-N_3 binding is reinforced by an additional weaker interaction through the carbonyl oxygen in the C_2 position.[27] It is now recognized that the 4-NH_2 group of cytosine, like the 6-NH_2 group of adenine and the 2-NH_2 group of guanine, is actually a poor ligand since its lone pair is involved in π delocalization and is unavailable for complexation.[28]

Acknowledgment. We gratefully acknowledge the help of NIH Grants CA-17367 and AM-15846, and RCD Award CA-00015, in support of this research.

References and Footnotes

(1) (a) J. J. Roberts and J. M. Pascoe, *Nature*, **235**, 282 (1972); (b) J. J. Roberts, in "Platinum Coordination Complexes in Cancer Chemotherapy", T. A. Connors and J. J. Roberts, Ed., Springer-Verlag, New York, N.Y., 1974.

(2) Interstrand cross-linking of DNA by cis platinum complexes has been shown to take place in vitro.[1] Although recent experiments have indicated that not all the biological effects of *cis*-$Pt(NH_3)_2Cl_2$ can be explained by this mechanism,[3] the cross-linking model is still a very attractive one because of the close similarities between certain properties of *cis*-$Pt(NH_3)_2Cl_2$ and the classical difunctional alkylating agents.

(3) (a) L. L. Munchausen, *Proc. Nat. Acad. Sci., U.S.*, **71**, 4519 (1974); (b) H. W. Van Den Berg, H. N. A. Fraval, and J. J. Roberts, *J Clin. Hematol. Oncol.* (Wadley Medical Bulletin), **7**, 349 (1977).

(4) For reviews of platinum complexes in cancer chemotherapy, see the following: (a) B. Rosenberg, *Naturwiss.*, **60**, 399 (1973); (b) M. J. Cleare and D. Hoeschele, *Bioinorg. Chem.*, **2**, 187 (1973); (c) J. L. Marx, *Science*, **192**, 744 (1976); (d) J. A. Gottlieb and B. Drewinko, *Cancer Chemother. Rep., Part 1*, **59**, 621 (1975).

(5) (a) Proceedings of the Third International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy, published as Volume 7 of the *J. Clin. Hematol. Oncol.* (Wadley Medical Bulletin), Jan. 1977; (b) "Platinum Coordination Complexes in Cancer Chemotherapy", T. A. Conners and J. J. Roberts, editors, Springer-Verlag, New York, N.Y., 1974.

(6) (a) L. L. Munchausen and R. O. Rahn, *Cancer Chemother. Rep., Part 1*, **59**, 643 (1975); (b) P. J. Stone, A. D. Kelman, F. M. Sinex, M. M. Bhargava, and H. O. Halvorson, *J. Mol. Biol.*, **104**, 793 (1976).

(7) C. R. Morris and G. R. Gale, *Chem. Biol. Interact.*, **7**, 305 (1973).

(8) The solution which results from the treatment of $Pt(amine)_2Cl_2$ with $AgNO_3$ was thought to contain primarily $[Pt(amine)_2(H_2O)_2]^{2+}$, but recent crystallographic evidence indicates that appreciable amounts of oligomeric species such as $[Pt(amine)_2(OH)]_2^{2+}$, $[Pt(amine)_2(OH)]_3^{3+}$, and $[Pt(amine)_2(OH)]_4^{4+}$ may also be present.[9]

(9) (a) R. Faggiani, B. Kippert, C. J. L. Lock, and B. Rosenberg, *J. Am. Chem. Soc.*, **99**, 777 (1977); (b) C. J. L. Lock, J. Bradford, R. Faggiani, R. A. Speranzini, G. Turner, and M. Zvagulis, *J. Clin. Hematol. Oncol.* (Wadley Medical Bulletin), **7**, 63 (1977).

(10) The major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. R. E. Marsh and his group at the California Institute of Technology. Scattering factors for Pt, P, O, N, and C were obtained from the "International Tables for X-ray Crystallography", The Kynoch Press, Birmingham, England, 1968. Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were applied to the platinum scattering factors. No attempt was made to locate the H atoms of the molecule.

(11) The x-ray diffraction patterns obtained from crystals of $[Pt(en)(5'\text{-CMP})]_2$ were very weak because of small sample size. Repeated attempts at recrystallization failed to yield larger crystals. Consequently the agreement factor in this structure analysis is somewhat higher than usual.

(12) The conformation about the exocyclic C_4'-C_5' bond, however, is different in the two molecules: In one CMP it is gauche,gauche, and in the other it is gauche,trans. For a definition of these and other conformational terms used in the text, see W. Saenger, *Angew. Chem., Int. Ed. Engl.*, **12**, 591 (1973).

(13) There is, however, a recent report of a platinum complex with 1-methylcytosine (C. J. L. Lock, R. A. Speranzini, and J. Powell, *Can. J. Chem.*, **54**, 53 (1976)). This structure shows unidentate cytosine-Pt bonding through the N_3 position, with a Pt-N_3 distance equal to that in $[Pt(en)(5'\text{-CMP})]_2$.

(14) J. A. Stanko, reported to the Second International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy, Oxford, England, April 1973. See p 25 of ref 5b.

(15) (a) A. B. Robins, *Chem. Biol. Interact.*, **6**, 35 (1973); (b) *ibid.*, **7**, 11 (1973).

(16) P. Horacek and J. Drobnik, *Biochim. Biophys. Acta*, **254**, 341 (1971).

(17) G. R. Clark and J. D. Orbell, *J. Chem. Soc., Chem. Commun.*, 697 (1975).

(18) R. Bau, R. W. Gellert, and J. K. Shiba, Abstracts of the Seventh International Conference on Organometallic Chemistry, Venice, Italy, 1975, p 238.

(19) R. W. Gellert and R. Bau, *J. Am. Chem. Soc.*, **97**, 7379 (1975).

(20) (a) P. L. Dahlstorm, R. E. Cramer, and M. Kashiwagi, Abstracts of the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., 1976, Abstract 124; (b) R. E. Cramer and P. L. Dahlstrom, *J. Clin. Hematol. Oncol.* (Wadley Medical Bulletin), **7**, 330 (1977).

(21) D. M. L. Goodgame, I. Jeeves, F. L. Phillips, and A. C. Skapski, *Biochim. Biophys. Acta*, **378**, 153 (1975).

(22) R. Bau, R. W. Gellert, S. M. Lehovec, and S. Louie, *J. Clin. Hematol. Oncol.* (Wadley Medical Bulletin), **7**, 51 (1977).

(23) (a) J. P. Davidson, P. J. Faber, R. G. Fischer, Jr., S. Mansy, H. J. Peresie, B. Rosenberg, and L. Van Camp, *Cancer Chemother. Rep., Part 1*, **59**, 287 (1975); (b) J. K. Barton, H. M. Rabinowitz, D. J. Szalda, and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 2827 (1977).

(24) C. J. L. Lock, R. A. Speranzini, G. Turner, and J. Powell, *J. Am. Chem. Soc.*, **98**, 7865 (1976).

(25) (a) J. A. Carrabine and M. Sundaralingam, *Chem. Commun.*, 746 (1968); (b) M. Sundaralingam and J. A. Carrabine, *J. Mol. Biol.*, **61**, 287 (1971); (c) K. Saito, R. Terashima, T. Sakaki, and K. Tomita, *Biochem. Biophys. Res. Commun.*, **61**, 83 (1974); (d) T. J. Kistenmacher, D. J. Szalda, and L. G. Marzilli, *Acta Crystallogr.*, **B31**, 2416 (1975); (e) D. J. Szalda, L. G. Marzilli, and T. J. Kistenmacher, *Inorg. Chem.*, **14**, 2076 (1975); (f) D. J. Szalda,

L. G. Marzilli, and T. J. Kistenmacher, *Biochem. Biophys. Res. Commun.*, **63**, 601 (1975).
(26) For a general review on structures of metal-nucleoside and metal-nucleotide complexes, see D. J. Hodgson, *Prog. Inorg. Chem.*, **23**, in press.
(27) There is, however, an exception to the N_3-binding rule for cytosine derivatives. In the structure of Mn(5'-CMP)·$2\frac{1}{2}H_2O$, cytosine was found to coordinate through O_2 (the carbonyl oxygen in the C_2 position) and not through N_3: K. Aoki, *Chem. Commun.*, 748 (1976).
(28) In over twenty structure determinations of metal complexes of adenine, guanine, and cytosine derivatives, complexation via an exocyclic amino group has never been found.[26]
(29) Alfred P. Sloan Fellow, 1974–1976; NIH Research Career Development Awardee, 1975–1980.

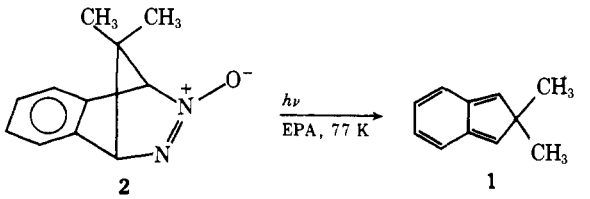
Samuel Louie, Robert Bau*[29]
Department of Chemistry
University of Southern California
Los Angeles, California 90007
Received January 21, 1977

2,2-Dimethylisoindene and 5,5-Dimethylbenzobicyclo[2.1.0]pent-2-ene

Sir:

While *o*-xylylene[1] and various *o*-xylylene derivatives[2] have been generated, isolated, and characterized spectroscopically, isoindenes have heretofore eluded isolation, although they have been demonstrated to exist as transient intermediates under various reactive conditions.[3]

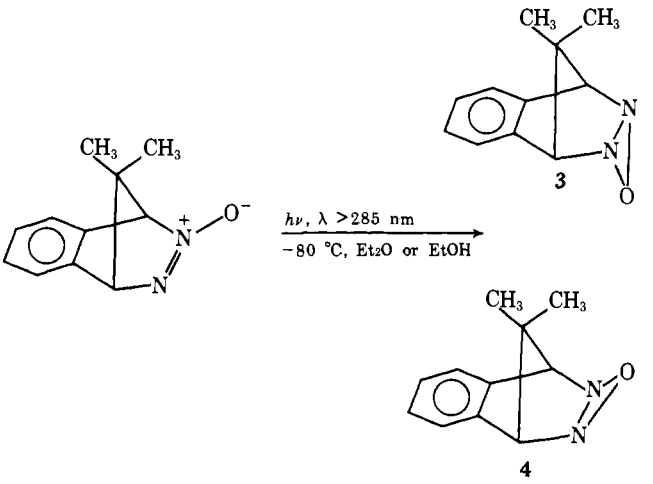
We have found that 2,2-dimethyl-2*H*-indene (2,2-dimethylisoindene), **1**, may be generated and isolated in an EPA glass matrix at 77 K by irradiation of azoxy compound **2**[3b] (high-pressure mercury lamp and $\lambda > 285$ nm filter, or low-pressure mercury lamp). **1** exhibited a structured absorption



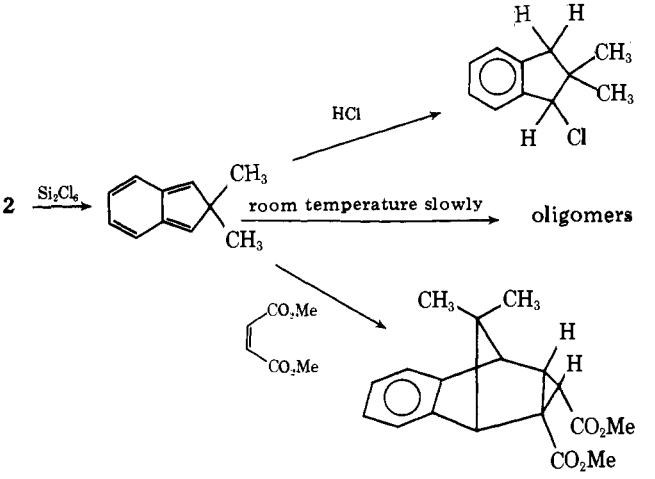
2 **1**

band (λ_{max} 405 nm) and a similarly structured light blue fluorescence (λ_{max} 467 nm) in a good mirror-image relationship. Both were quite similar to the spectra reported for alkyl substituted orthoxylylenes[2a] as well as for *o*-xylylene itself,[1] but were red-shifted by about 2000 cm^{-1}, presumably due to cyclic hyperconjugation. The shape of the emission curve of **1** is independent of excitation wavelength and the excitation spectrum follows the shape of the absorption band. The onsets of absorption and emission almost coincide, and the 0-0 bands are clearly discernible as relatively intense peaks (λ_{max} (A) 432 nm and λ_{max} (E) 439 nm). As in the case of other reported spectra of *o*-xylylenes,[1,2] the calculated (PPP) first transition is allowed and occurs near the observed position, and a very weak transition into a predominantly doubly excited state at somewhat higher energies is apparently buried under the first band.

While **1** was found to be stable indefinitely at room temperature in EPA solution, it was produced only in very small quantities upon irradiation ($\lambda > 285$ nm) of **2** at 25 °C or even at −80 °C. At the latter temperature there was a smooth conversion to species containing the benzene chromophore and isomeric with **2**, stable for days at −80 °C but reconverting to **2** in several hours upon warming to −20 °C. NMR (CD_3OD) showed that two photoisomers were formed in a ratio of about 2.5:1. Both contribute to a narrow multiplet at δ 7.38 (4 H); the major isomer also has singlets at δ 4.64 (2 H), 1.50 (3 H), and 0.57 (3 H), the minor isomer also has singlets at δ 4.81 (2 H), 1.44 (3 H), and 0.60 (3 H). Thus, the probable solution photoproducts are endo and exo oxadiaziridines, **3** and **4**. Greene and Hecht have previously demonstrated the ability of azoxy compounds to cyclize in this manner.[4]



In view of the apparent ability of the *gem*-dimethyl substituents to stabilize the isoindene toward oligomerization, we attempted to generate **1** at room temperature by an alternative method. Thus, it was found that **2** underwent deoxygenation by Si_2Cl_6[5] followed by loss of N_2 from the probable transient azo compound to produce **1**.



The NMR spectrum of the bright yellow solution (100 MHz) showed a singlet at δ 1.16 (6 H) and vinylic multiplets at δ 6.08 (4 H) and 6.55 (2 H). This is the first reported NMR spectrum for an *o*-xylylene derivative, although NMR spectra have been obtained for *p*-xylylene,[6] isoindole,[7] isobenzofuran,[8] and for 1,2-(2,3-naphtho)-*o*-carborane.[9] The reported chemical shift for ring protons of *p*-xylylene (δ 6.49) is indicative of a similar lack of aromaticity in ortho and *p*-xylylene-type molecules. The yellow color of the isoindene was rapidly discharged when the solution was treated with either HCl or dimethyl maleate with products **5** and **6** being formed, isolated, and characterized by comparison with authentic samples.

When a fluid isoindene solution in various solvents was irradiated at 0 °C or below, it rapidly lost its color. When warmed to room temperature, the color soon reappeared. An NMR analysis of this photolytic-thermal interconversion in Si_2Cl_6 showed that 5,5-dimethylbenzobicyclo[2.1.0]pent-2-ene was the photoproduct. **7** gave an NMR with singlets at δ 0.94