Nb–Cl_c, 2.468 [4] Å; Nb–Cl_b(trans to P), 2.529 [4] Å; Nb–Cl_b(trans to Cl), 2.474 [4] Å; Nb–Cl_t, 2.483 [7] Å; Nb–P(trans to Cl_b), 2.695 [2] Å; Nb–P(trans to Cl_c), 2.729 [7] Å; where subscripts c, b, and t refer to capping, bridging, and terminal chlorine atoms, respectively. The metal–ligand distances show trans influences: Nb–Cl_b trans to P is longer than Nb–Cl_b trans to Cl_t and Nb–P trans to Cl_c is longer than Nb–P trans to Cl_b.

The cluster has eight electrons in the M_3 core, and based upon the electronic configuration of the M_3X_{13} molecules (vide infra), it is expected to have a singlet ground state and consequently be diamagnetic. This was confirmed by the determination of its magnetic susceptibility[9] which gave a value of χ_M equal $-(560 \pm 60) \times 10^{-6}$ cgs at room temperature. The proton NMR spectrum[10] of the complex was uninformative, with unresolved peaks for both phenyl and methyl protons. Proton-decoupled phosphorus-31 signals were observed[11] only at low temperatures. The spectrum recorded at −90 °C in THF consisted of a sharp peak at −46 ppm due to free phosphine and two broad resonances centered around −10 and −3.5 ppm due to the inequivalent sets of coordinating phosphines. While the width of the signals may to some degree result from partial substitution of the ligands by the solvent (thus giving a number of mixed THF/phosphine species), we believe that the broadening is mainly or entirely due to the quadrupolar moment of ^{93}Nb nuclei. This nuclide has been reported[12] to cause anomalous and unexpected effects in the NMR spectra of some compounds of Nb. Analogous V and Ta species did not exhibit such problems. In general it is not possible to predict in which compounds the interaction with Nb nuclei is going to affect the NMR behavior since the phenomenon is not well understood. Clearly, the preparation and investigation of the Ta trimers would shed some light on this problem.

The compound reported here differs from Nb_3Cl_8 in the number of electrons present in the Nb_3 cluster, but the difference is consistent with a long-established understanding of the electronic structures of compounds with this type of structure.[13] The molecular orbitals that can be assigned primarily metal atom cluster character (in contradistinction to metal–ligand or ligand character) are three: an e and an a_1 orbital which correspond to three M–M σ bonds and another a_1 orbital of somewhat higher energy that is approximately nonbonding in the M–M sense. On this basis, the ideal population of the cluster would be six electrons, which would occupy the e and lower a_1 bonding MO's. However, one or two more more electrons can be accommodated without severely destabilizing the structure.[14] In the case of Nb_3Cl_8 there are seven electrons and in the type of compound described here there are eight.

The reported[1] dimensions of Nb_3Cl_8, which has crystallographically imposed $3m$ symmetry, are Nb–Nb, 2.810 Å; Nb–Cl_c, 2.438 Å; Nb–Cl_b, 2.428 Å; and Nb–Cl_t, 2.634 and 2.522 Å. In this case the metal–metal and metal-capping chlorine distances are somewhat shorter than in the phosphine complex. Such small differences may arise from several sources: the fact that in Nb_3Cl_8 the Cl atoms belong to a continuous array and are shared between clusters; the presence of some phosphine ligands in place of Cl^- ligands; the occurrence of different numbers (seven and eight) of cluster electrons.

Preliminary results obtained with other phosphines indicate the formation of trinucler clusters analogous to the PMe_2Ph complex. In particular the use of PBu_3 followed by reaction of the product with dmpe, bis(dimethylphosphino)ethane, afforded an analogous trinuclear compound with bidentate ligands chelating the Nb atoms.

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Supplementary Material Available: Tables of positional and isotropic-equivalent thermal parameters, bond distances, and bond angles for $Nb_3Cl_7(PMe_2Ph)_6 \cdot C_7H_8$ (6 pages). Ordering information is given on any current masthead page.

(9) A magnetic susceptibility balance manufactured by Johnson Matthey Inc. was used.

(10) Proton NMR spectra were recorded on a Varian XL-200 spectrometer using CD_3CN as solvent.

(11) $^{31}P\{H\}$ spectra were recorded on a Varian XL-200 spectrometer operating at 80.984 MHz with H_3PO_4 as the standard for chemical shifts.

(12) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1982, vol. 3, pp 707–708.

(13) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 1217.

(14) Several examples of eight-electron systems containing $Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3$ cores have been reported, namely, $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]ClClO_4$[15] and $(Et_4N)_2[Mo_3OCl_8(O_2CCH_3)_2]$.[16]

(15) Bino, A.; Cotton, F. A.; Dori, Z. *Inorg. Chim. Acta* **1979**, *33*, L133.

(16) Shang, M.; Huang, J.; Liu, J. *Acta Crystallogr., Sect. C* **1984**, *C40*, 761.

DNA, Light, and Dewar Pyrimidinones: The Structure and Biological Significance of TpT3

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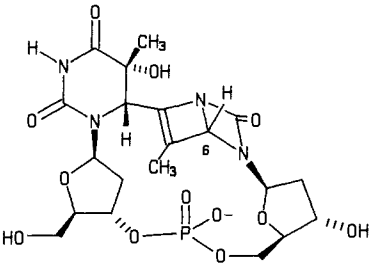
The cis-syn and (6-4) dipyrimidine photodimers are the major products produced by irradiation of DNA at 254 nm and are considered to be the principal photolesions leading to mutation and cancer by ultraviolet light.[1,2] The existence of perhaps another biologically relevant class of lesions comes from reports in the early 1970s of type III photoreactivation of the lethal effects of 254-nm light on a variety of bacterial strains.[3] Type III photoreactivation was shown to be most efficient at 313 nm and to proceed through an unknown, though nonenzymatic, pathway which was correlated with the disappearance of (6-4) products. Interestingly, in 1964 Johns et al. had reported that the (6-4) product of TpT, known to them only as TpT4, could be converted quantitatively at 313 nm to a new photoproduct, TpT3, and back again at 240 nm (see Scheme I).[4] Such photochemical behavior is quite similar to that observed for simpler pyrimidinones which have been shown to be photoisomerized to their Dewar isomers at wavelengths greater than 300 nm.[5] Herein we report the remarkable structure of TpT3, which we have determined to contain a highly strained



TpT3

Dewar pyrimidinone subunit and which we show can be produced by direct photolysis of TpT with biologically relevant wavelengths of light.

(1) See: (*a*) Friedberg, E. C. *DNA Repair*; Freeman, New York, 1985. (b) Wang, S. Y., Ed. *Photochemistry and Photobiology of Nucleic Acids*; Academic: New York, 1976; Vols. I and II.

(2) For a recent review of the role of (6-4) products in ultraviolet light induced transition mutations, see: Franklin, W. A.; Haseltine, W. A. *Mutat. Res.* **1986**, *165*, 1–7.

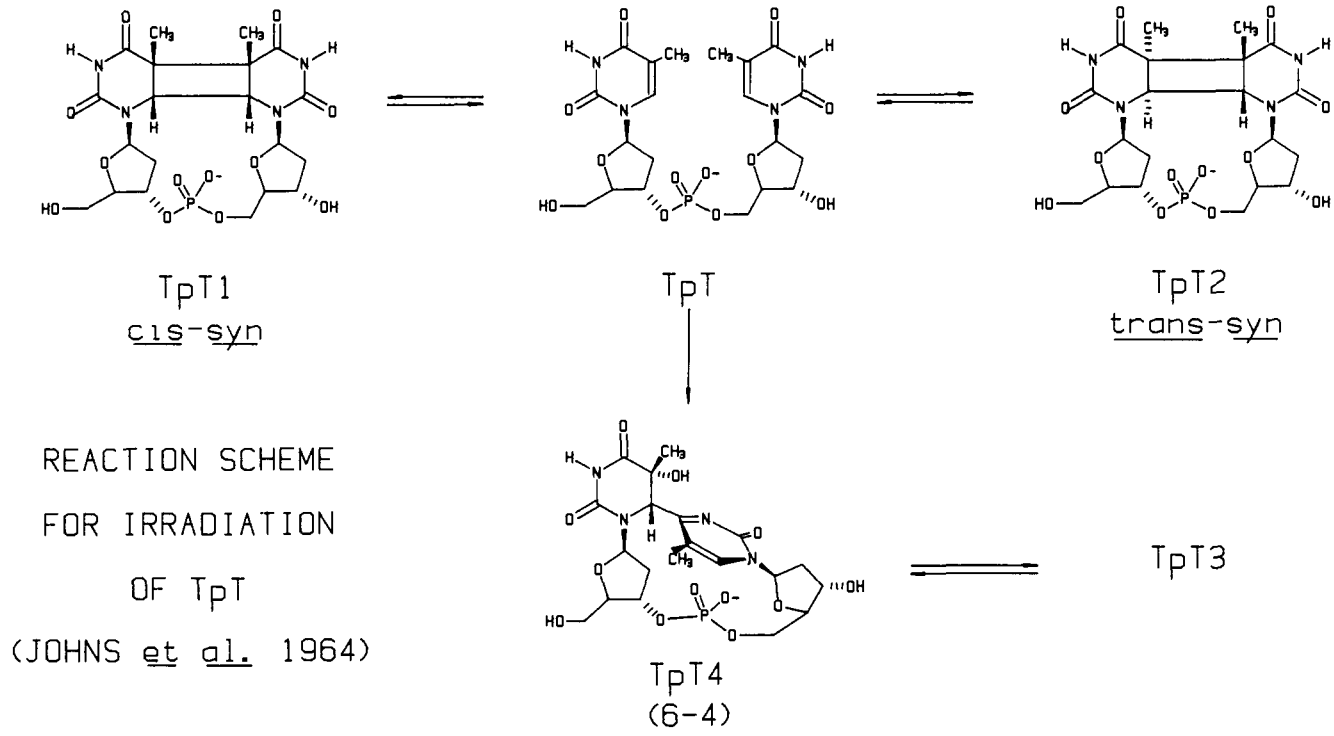
(3) (a) Patrick, M. H. *Photochem. Photobiol.* **1970**, *11*, 477–485. (b) Ikenaga, M.; Patrick, M. H.; Jagger, J. *Ibid.* **1970**, *11*, 487–494. (c) Jagger, J.; Takebe, H.; Snow, J. M. *Ibid.* **1970**, *12*, 185–196. (d) Ikenaga, M.; Patrick, M. H.; Jagger, J. *Ibid.* **1971**, *14*, 175–187.

(4) Johns, H. E.; Pearson, M. L.; LeBlanc, J. C.; Helleiner, C. W. *J. Mol. Biol.* **1964**, *9*, 503–524.

(5) (a) Nishio, T.; Katoh, A.; Omote, Y.; Kashima, C. *Tetrahedron Lett.* **1978**, 1543–1544. (b) Nishio, T.; Kato, A.; Kashima, C.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1980**, 607–610.

0002-7863/87/1509-2834$01.50/0

Scheme I



TpT3 was produced in quantitative yield by irradiation of the (6-4) photoproduct of TpT[6] with Pyrex-filtered medium-pressure mercury arc light. The key spectroscopic evidence in support of our proposed structure for TpT3 is as follows:[7] (1) the molecular weight is identical with that of the (6-4) photoproduct,[8] (2) the 326-nm UV absorption maxima, characteristic of the pyrimidinone ring of the (6-4) product,[4,6] is no longer present, (3) a new IR absorption band appears at 1780 cm^{-1} which is typical of Dewar pyrimidinones,[5] (4) the NMR chemical shift of the pTH_6 proton is 5.28 ppm, 2.67 ppm upfield from that found for the (6-4) product,[6] (5) the NMR chemical shift of the pTC_6 carbon has also moved upfield, from 146.9 ppm found for that of the (6-4) product[6] to 72.3 ppm, (6) the pTC_6–H_6 coupling constant is 184 Hz, which is consistent with that expected for a saturated carbon within a small-membered ring heterocycle.

In order to determine whether or not TpT3-type products might be produced by direct exposure of DNA to biologically relevant wavelengths of light, i.e., wavelengths greater than 280 nm, TpT was irradiated with Pyrex-filtered medium-pressure mercury arc light. Analysis by both ^{31}P (Figure 1) and ^{1}H NMR clearly indicated the production of TpT3, in addition to the cis-syn and trans-syn photoproducts. As expected from the work of Johns et al.,[4] no (6-4) photoproduct was detected.[9] This suggests that (6-4) photoproducts produced during exposure of DNA to sunlight might be converted primarily to their Dewar valence isomers. We have found TpT3 to be stable in aqueous solution for months at room temperature, suggesting that such lesions might persist for long periods of time in vivo.

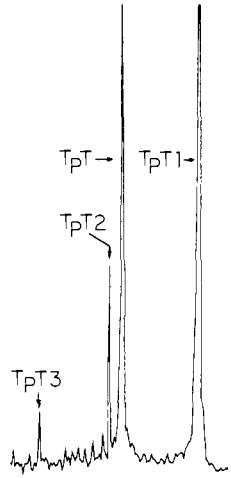


Figure 1. ^{31}P spectrum, 121.5 MHz, of the reaction mixture resulting from exposure of TpT to Pyrex-filtered medium-pressure mercury arc light.

We are currently exploring the chemistry of this new class of highly strained photoproducts and developing ways to site-specifically incorporate them into DNA in order to determine their role in sunlight-induced mutagenesis and type III photoreactivation. Because of the known susceptibility of the carbonyl of Dewar pyrimidinones to nucleophilic attack,[5b] we are also investigating the extent to which TpT3-type lesions might be involved in suicide enzyme inactivation of DNA processing enzymes or in DNA–DNA and DNA–protein crosslinking.

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(6) (a) Rycyna, R. E.; Alderfer, J. L. *Nucleic Acids Res.* **1985**, *13*, 5949–5963. (b) Taylor, J.-S.; Wang, M. J.; Garrett, D. S., unpublished results.

(7) NMR chemical shifts are for the ammonium salts in D_2O at 30 °C relative to external sodium 3-(trimethylsilyl)-1-propanesulfonate. The NMR assignments reported are based on the results of extensive 1D and 2D NMR experiments which will be presented in full detail elsewhere. NMR data not reported are also consistent with the proposed structure. The stereochemistry of the bridgehead carbon of the Dewar pyrimidinone, pTC_6, was determined by model building based on NOEs observed between the $pTCH_3$ and pTH_6 protons and various sugar ring protons (pT refers to the thymidine 5′-phosphate subunit).

(8) High-resolution FABMS: Calcd for $C_{20}H_{26}N_4O_{12}P$ 545.1280, found 545.1294.

(9) TpT3 and the (6-4) product of TpT have almost identical ^{31}P shifts[6] and were distinguished by the ^{1}H NMR shifts of their methyl signals.