tiomers since the "Pt(*trans*-dach)" moiety possesses pseudo-twofold rotational symmetry. Both of the ascorbate chelates [Pt(*trans*-(*R,R*)-dach)(ascorbate)]·$3H_2O$ (**4**)[6] and [Pt(*trans*-(*S,S*)-dach)(ascorbate)]·$2H_2O$ (**5**)[13] have been isolated as pure components and shown to be structurally analogous to the crystallographically characterized [Pt(*cis*-dach)(ascorbate)] analogue **1** by using NMR spectroscopy. While the individual diastereomeric forms of the bis(ascorbate) component [Pt(*trans*-dach)(ascorbate)$_2$]·$2H_2O$ (**6**) have yet to be isolated, chemical analysis of the mixed *R,R* and *S,S* forms of **6**[12] is in agreement with the proposed chemical formulation.

These novel complexes of vitamin C are the first carbon-bound analogues of *cis*-diamineplatinum(II) to display good antitumor activity in vivo. We are presently examining a number of related compounds to determine structure–activity relationships among complexes in this potentially broad class of new antitumor agents.

Supplementary Material Available: Listings of bond lengths and angles (Table S1) and atomic positional and thermal parameters (Table S2) for compound **1**, and ^{195}Pt and ^{13}C NMR data (Tables S3 and S4) for compounds **1–5** (4 pages). Ordering information is given on any current masthead page.

(13) Anal. ($PtC_{12}H_{24}N_2O_8$) Pt, C, H, N.

Picosecond Absorption Studies on *m*-Naphthoquinomethane. Singlet–Triplet Intersystem Crossing

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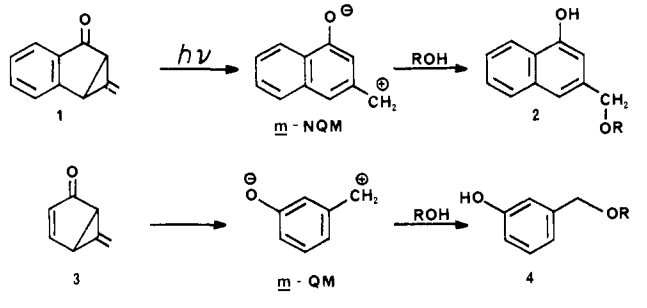
We report the use of picosecond flash photolysis to investigate the chemical dynamics of *m*-naphthoquinomethane (*m*-NQM), a member of the meta quinonoid series of non-Kekulé molecules.[2] That this species has a triplet ground state is suggested by a semiempirical molecular orbital calculation[3] and is confirmed experimentally[2a] by electron paramagnetic resonance (EPR) spectroscopic studies of immobilized samples at 77 K. In chemical reactions, *m*-NQM and its close relative *m*-quinomethane (*m*-QM) behave as dipolar intermediates and readily add nucleophiles such as amines, electron-rich olefins, and alcohols.[2a] The alcoholyses give high yields of phenolic ethers **2** and **4**. Although the evidence[4]



favors singlet *m*-NQM and *m*-QM, respectively, as the *first-formed* intermediates in the photolysis or pyrolysis of the precursors **1** and **3**, the spin state of the reactive form has not been clearly established.

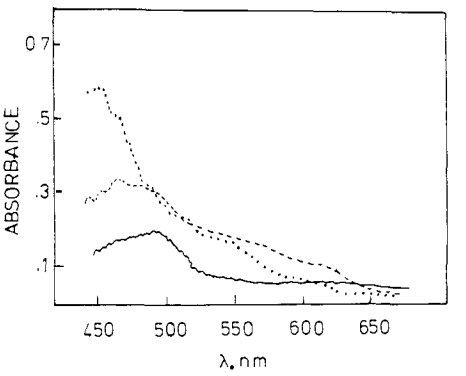


Figure 1. Spectra observed 25 ps after 355-nm excitation of **1** in cyclohexane (—), benzene (- - -), and acetonitrile (·····).

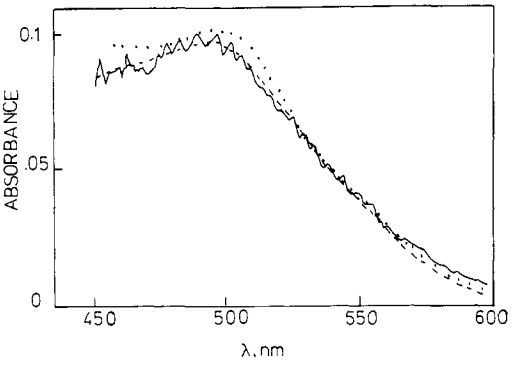


Figure 2. Spectra observed 9 ns after 355-nm excitation of 1 in cyclohexane (—), benzene (- - -), and acetonitrile (·····). The spectra have been redrawn to scale.

The experimental procedure for obtaining absorption spectra of transient intermediates with a time resolution of 25 ps has been previously described in detail.[5] Photolysis was performed at 355 nm on room temperature $\sim 5 \times 10^{-3}$ M solutions of **1** (OD $\geq$ 1.5). The photolyzed solutions were frequently changed (<3000 laser shots) to prevent the buildup of photoproducts.

Photolysis of **1** in several different solvents produces a transient intermediate (A) within the laser pulse. Although the overall shape of the spectrum does not vary greatly, the maximum of A (Figure 1) changes dramatically with the polarity of the solvent: 490 (cyclohexane), 470 (benzene), <450 nm (CH_3CN). The transient A decays on the picosecond time scale to a new species (B), which is stable onto the nanosecond timescale. The absorption spectrum of B (Figure 2) at 9 ns shows λ_{max} = 500 nm and is insensitive to solvent polarity in the observable region. Importantly, the same species is produced in all three solvents. The insensitivity of the absorption spectrum of B at 9 ns suggests that A has largely disappeared.

The reaction of A → B in the three solvents follows first-order kinetics as monitored by absorption spectroscopy at several wavelengths >525 nm. Measurements between 25 ps and 9 ns give $1/k$ = 250 ± 100 ps (cyclohexane), 750 ± 350 ps (benzene), and 2.74 ± 1.1 ns (CH_3CN). Pseudo-first-order reaction between **1** and A to give B requires implausibly large concentration and/or reaction rate for A and in any case is ruled out by the insensitivity of the observed rate constant to variation in the initial concentration of **1**.

Disappearance of A in benzene in the presence of a large excess of methanol follows pseudo-first-order kinetics. A plot of k_{obsd} vs. [CH_3OH] is linear (r = 0.997) with an intercept $k_1 = 8.5 \times 10^8$ s^{-1} and a slope corresponding to a second-order rate constant $k_2 = 3.6 \times 10^8$ s^{-1} M^{-1}. In pure methanol, neither the A nor B signal appears. The kinetic data may be expressed as $k_{obsd} = k_1$

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+ k_2[CH_3OH] and suggest that A undergoes a unimolecular decay to form B in the absence of methanol, but when methanol is present, A is intercepted competitively to produce a species with no absorption in the region 450–750 nm.

The optical spectrum of *m*-NQM in cryogenic matrices shows a long-wavelength transition that is associated with the carrier of the characteristic EPR spectrum of the triplet biradical.[3] The position of this band is insensitive to the medium: λ_{max} = 500 (EtOH), 504 nm (5:1 isopentane/Et_2O). These features match those of the present transient B and support its assignment as triplet *m*-NQM.

Although the spectroscopic data alone do not exclude an excited state of ketone **1**, this alternative seems unlikely because the chemistry of the *m*-NQM[2a] and *m*-QM[2a,4] intermediates is independent of whether they are thermally or photochemically generated.[6] The most probable assignment of the A signal thus is to singlet *m*-NQM, and the unimolecular decay A → B measures the intersystem crossing (isc). Increases in isc rate with decreased solvent polarity, similar to those observed here, have been noted in other systems.[7,8]

The present observations constitute the first direct evidence for a cascade of states in the generation of *m*-naphthoquinomethane and identify singlet *m*-NQM as the reactive intermediate in the photomethanolysis of ketone **1**.

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(6) Fluorescence during the lifetime of the A signal was not observed, which would be difficult to rationalize if the A signal were assigned to excited singlet **1**. Moreover, A is unlikely to be the n,π^* triplet **1**, since that species would be expected to react with alcohols (by hydrogen abstraction) with rate constants[9] near 10^6 s^{-1}, about 100-fold slower than the k_2 observed here.

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A Molecular Beam of Tryptophan

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We report here the production of a supersonic molecular beam of the amino acid tryptophan. The significance of this report is that it demonstrates that a cold molecular beam of neutral molecules can be produced from a thermally labile nonvolatile solid. If the technique described in this communication proves to be generally applicable, it will allow the study of individual molecules of materials that ordinarily exist only as solids or in solution and will make it possible to distinguish intrinsic properties of single molecules from their properties in condensed phases.

In the past we have made extensive use of supersonic molecular beams to prepare gas-phase samples for study by electronic spectroscopy.[1] The supersonic expansion cools the vibrational and rotational degrees of freedom of the molecule without causing condensation out of the gas phase, and the electronic spectra of internally cold, isolated, gas-phase molecules have proven to be quite informative in many cases. To be suitable for supersonic beam spectroscopy, a molecule of interest must have a sufficiently high vapor pressure. In cases where the room temperature vapor pressure is too low, the necessary volatility has been produced by heating the sample prior to cooling it in the supersonic expansion;[2] however, many solids thermally decompose at tempertures where the vapor pressure is still far below that necessary for molecular beam spectroscopy. The present work was motivated by the desire to prepare molecular beams of such substances.

Mass spectroscopists face a similar problem. In recent years they have developed a number of ingenious techniques to volatilize large organic molecules,[3] particularly appealing methods being electrospray[4] and the thermospray technique developed by Vestal and co-workers.[5] We have combined a thermospray jet and a seeded supersonic helium expansion to produce a molecular beam of tryptophan. Our method involves injecting a thermospray jet of a methanol solution of tryptophan into the throat of a pulsed nozzle producing a seeded supersonic free jet in a helium carrier gas. The free jet is skimmed, and the resulting molecular beam is directed into a time-of-flight mass spectrometer where the isolated, neutral tryptophan molecules are nonresonantly photoionized. The existence of a cold molecular beam of neutral tryptophan is inferred from analysis of the mass spectrum.

The thermospray jet is formed by continuously passing a 10^{-4} M solution of DL-tryptophan in methanol through a 0.004-in.-i.d. stainless steel capillary which terminates in a 35-μm nickel pinhole.[6] The last few centimeters of the capillary pass through a brass block that is heated by electric resistance heaters. The temperature of the block is chosen so that the interface between the liquid and vaporized solvent occurs just behind the pinhole, and this temperature is dependent on the pressure that is used to drive the solution through the capillary and pinhole. We typically use a pressure of ~10 atm, producing a solution flow rate of ~0.2 mL/min at a block temperature of ~200 °C.

The molecular beam is formed by using a solenoid actuated pulsed valve that discharges the helium carrier gas at a stagnation pressure of ~2 atm into a 1 mm diameter × 9 mm long cylindrical channel in the brass block. The valve pulse width is adjustable down to a few hundred microseconds. The thermospray jet is continuously injected into the middle of the helium channel with the flow axis of the thermospray perpendicular to that of the helium expansion. A 0.2 mL/min flow of a 10^{-4} M solution of tryptophan in methanol corresponds to a flow of 8×10^{-5} mol/s of methanol and 3×10^{-10} mol/s of tryptophan. The measured average flow rate of helium is 140 mtorr L/s, and the duty cycle was 2×10^{-3} (200-μs pulse width × 10 Hz) implying a flow rate of 70 torr L/s or 4×10^{-3} mol/s when the valve is open. If the helium pulse contains only methanol and tryptophan that are injected while the pulse passes the thermospray jet, then the molecular beam would be formed from helium containing 2 mol % methanol and 10^{-5} mol % tryptophan. However, it may well be that methanol and tryptophan thermosprayed prior to the opening of the helium valve manage to penetrate the shock structure of the expanding helium, producing a molecular beam richer in seed molecules than that calculated above.

The helium–methanol–tryptophan free jet is skimmed by a 1-mm conical skimmer, and the resulting molecular beam is passed through a time-of-flight mass spectrometer having a triple grid ion extraction region,[7] an einzel lens, a 1-m flight tube, and a microchannel plate electron multiplier.[8] Photoionization is

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