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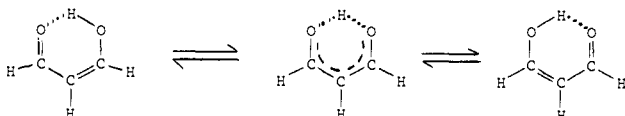
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$1^1B_1(n\pi^*) \leftarrow 1^1A_1$ Transition of Malondialdehyde¹

Sir:

The chemical composition of malondialdehyde, $(CHO)_2CH_2$, makes this molecule an important candidate for detailed spectroscopic studies of the quasi-symmetric hydrogen bond.²⁻⁵ The rovibronic ground state of the molecule has recently been found²⁻⁴ to be planar and intramolecularly hydrogen bonded. Hydrogen-bond proton tunneling apparently occurs through a rather low potential barrier which separates the two asymmetrical forms of the molecule. Recent theoretical work^{5,6}



suggests that this potential barrier should be significantly increased in the lowest energy singlet excited state in which the $n\pi^*$ configuration dominates (1^1B_1). Chemical rationale for the increased barrier height resides in decreased electron density on the "lone-pair" oxygen atom relative to the ground electronic state (1^1A_1). Thus, the strength of the hydrogen

Table I. 185-cm⁻¹ Progression in Malondialdehyde Vapor

Band position, cm ⁻¹ , air	Rel intensity	Band position, cm ⁻¹ , air	Rel intensity
27797	2	28719	5
27972	5	28898	3
28157	7	29082	2
28341	10 (max)	29295	1
28527	9		

bond to the oxygen atom is expected⁵⁻⁸ to be less and the energy barrier separating asymmetrical forms increased.

We have recently measured the $1^1B_1(n\pi^*) \leftarrow 1^1A_1$ electronic band system in the normal isotopic vapor of malondialdehyde and find it to contain ~ 150 vibronic components. There is apparently no other small molecule with a quasi-symmetric⁵ hydrogen bond where rovibronic definition in the spectrum will permit detailed interpretation of structural dynamics. Further, this is also the first reported instance of the measurement of a highly structured $\pi^* \leftarrow n$ transition in a small organic molecule in which there is an intramolecular hydrogen bond in the vapor phase monomer.

Malondialdehyde was synthesized as previously reported⁵ and extensively purified by vacuum sublimation immediately prior to measurements. Medium-resolution mass spectrometry identifies the molecular mass as 72. The crisp rotational contours and the similarity to an acetylacetone spectra of the banded infrared spectrum of the vapor strongly suggest a planar molecular geometry. Thus, our data support the microwave²⁻⁴ identification of the structure of the monomeric species. The $1^1B_1(n\pi^*) \leftarrow 1^1A_1$ transition was measured under medium (~ 5 cm⁻¹) resolution at 300 K. A White-Herzberg^{9,10} multiple-reflection gas cell set at 48-m optical path length was employed.

The most intense portion of the spectrum ($3630 \text{ \AA} > \lambda > 2950 \text{ \AA}$) is clearly evident at 5 Torr·m pressure-path length. The bulk of the total intensity consists of five repetitions of a prominent cluster of vibronic bands. Figure 1 shows the most intense such group of bands. These clusters appear at intervals of 1297 ± 10 cm⁻¹. It is likely that the 1297-cm⁻¹ interval corresponds to the 1^1B_1 state totally symmetric carbonyl stretching frequency reduced from 1661 cm⁻¹ (Q branch) in the 1^1A_1 state. Within each cluster of vibronic bands, an apparent progression of bands in 185 ± 10 cm⁻¹ is found. These bands are marked in Figure 1 and given in Table I. There are two likely explanations for the 185-cm⁻¹ intensity: first, a simple progression in 1^1B_1 state totally symmetric 185-cm⁻¹ vibration, and, second, a progression in an upper-state nontotally symmetric (b_2 in G_4) vibration⁵ originating from alternate levels of a ground-state (near) degenerate vibrational level pair

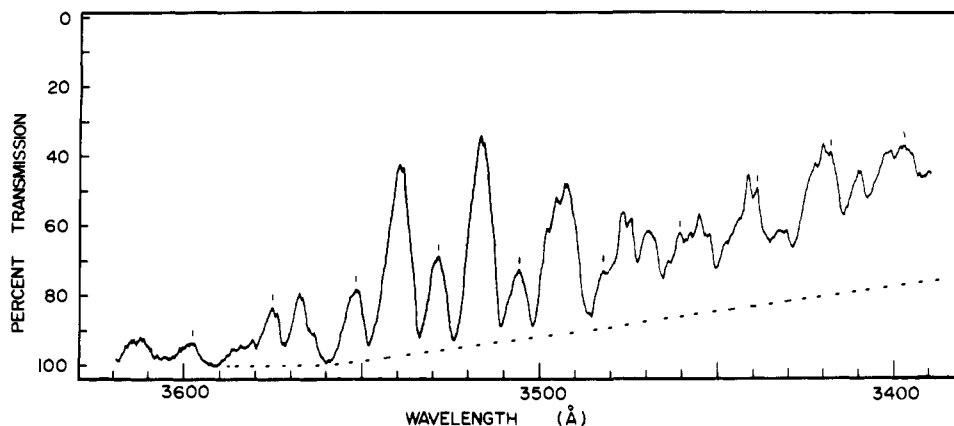


Figure 1. The medium resolution absorption spectrum of 100-mTorr malondialdehyde vapor at 48-m pathlength and 300 K. The dashed line denotes baseline absorption of the gas cell. Vertical hash marks denote bands forming a 185-cm⁻¹ progression.

(${}^e\nu A_1$ and ${}^e\nu B_2$). The latter identification requires that transitions terminate on alternating ${}^e\nu B_1$, ${}^e\nu A_2$ vibronic levels which are (approximately) evenly spaced; i.e., they lie above the 1^1B_1 state double-minimum potential barrier for the b_2 vibration. Both explanations require that the intensity be uniformly c type (out of plane). We currently prefer the second interpretation since it is consonant with microwave²⁻⁴ estimates of low-frequency 1^1A_1 state vibrational fundamentals. Isotope substitution and temperature studies now in progress will resolve this matter.

The integrated intensity of this band system—as indicated by the pressure–pathlength necessary for observation—is consistent only with an $\pi^* \leftarrow n$ transition in the molecule. The lack of a prominent origin band (ν_{00}) is corroborative evidence for such an orbital designation. The energy of the measured transition is in agreement with our published⁵ computational value of 3.2 eV and also that of Del Bene⁶ for the $1^1B_1(n\pi^*) \leftarrow 1^1A_1$ transition in the planar molecule. Taken as a whole, the evidence for the measured band system being attributable to the intramolecularly hydrogen-bonded planar molecule is conclusive. Studies of the high-resolution infrared and electronic spectra of isotopes of malondialdehyde are in progress.

References and Notes

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Free-Radical Participation in the Insertion Reaction of Acetylene with Platinum Hydride

Sir:

Previously we have demonstrated that the reaction of acetylenes with *trans*-PtHCl(PtEt₃)₂ (I) in polar solvents such as methanol or acetone proceeds with the displacement of the chloride ligand by the acetylene, followed by a migratory insertion of acetylene into the Pt–H bond (eq 1–3).¹

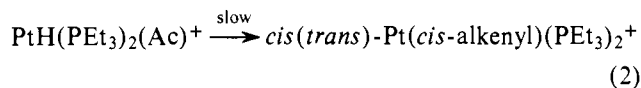


Table I. Reaction of PtHCl(PtEt₃)₂ with DMA in Benzene

[I], M	[DMA], M	Initiator	Inhibitor	Temp, °C	Reaction time, hr	Total % yield	Relative % yield			
							IIa	IIb	IIc	IId
0.42	0.42			Room	~10 days	74	85		15	
0.22	0.25			70	29	73	38		62	
1.4	1.6			70	21	78	92		8	
0.22	0.25		Hydroquinone (11 mol %)	70	43	82	36	37	27	
0.22	0.25		Hydroquinone (25 mol %)	70	45	86	42	41	17	
1.1	1.35	BPO (50 mol %)		Room	10	69	32		46	22
0.85	0.98	DBPO (5 mol %)		Room	1	81			58	42
0.85	0.98	APO (50 mol %)		Room	20	77	2	20	53	25

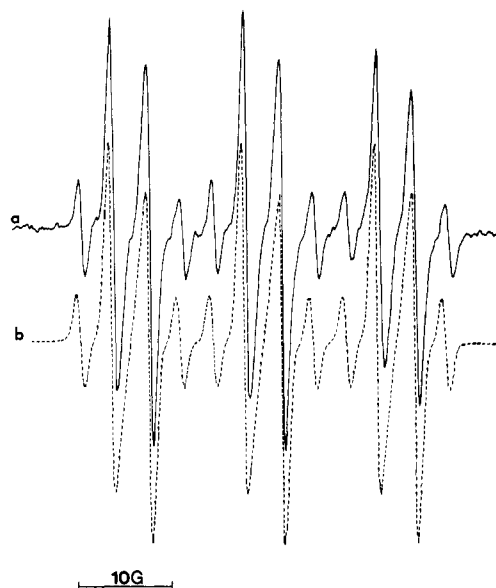
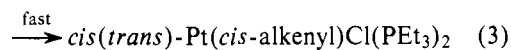
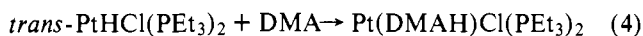


Figure 1. a (full line), the ESR spectrum of the spin adduct obtained by heating pheny-*tert*-butylnitron with PtHCl(PtEt₃)₂ and DMA in benzene at 70 °C; b (broken line), a computer-simulated spectrum using the hyperfine splittings $A_N = 14.32$, $A_H = 4.1$, and $A_{Pt} = 6.6$ G.



The vinylic complexes so formed have exclusively the *cis* arrangement of Pt and the vinylic proton about the alkenyl double bond. Thus I reacts completely with dimethylacetylenedicarboxylate (DMA) (eq 4)



IIa, *cis,cis*^{2,3}

b, *trans,cis*

c, *cis,trans*

d, *trans,trans*

in methanol within minutes of mixing at room temperature to give exclusively IIa. However, the same reaction in benzene takes more than a week for completion (Table I) with IIa as the major product plus a small amount of the *trans,trans* isomer IId. The percentage of IId increased significantly⁴ when the reaction temperature was 70 °C, and interestingly an increase in acetylene concentration caused a decrease in the percentage of the *trans*-alkenyl product.

The dependence of the product geometry on the polarity of the solvent medium led us to suspect that different mechanisms might be operative. Reaction 4 was therefore performed in the presence of free-radical initiators such as benzoyl peroxide (BPO), acetyl peroxide (APO), and di-*tert*-butyl peroxyoxalate (DBPO). Not only were reaction times shortened, but the percentage of the *trans*-alkenyl product increased to 68, 78,