cm^{-1}, but it is presumably weak (similar to that for CCO[4]) and was not observed. Table I gives the four isotopically substituted molecules for which the one stretching frequency of C_3O was definitely observed.

Table I. Force Constants (mdyn/Å) and Calculated Stretching Frequencies for the CCCO Molecule

$f_{C_1C_2} = 14.318$ $f_{C_3O} = 16.548$ $f_{C_1C_2-C_3O} = (1.29)^a$
$f_{C_2C_3} = 10.771$ $f_{CC-CC} = (2.37)^a$

	Frequency, cm^{-1}			
	Obsd	Calcd		
Molecule	ν_3	ν_3	ν_1	ν_2
12-12-12-16	2244	2245.5	2003.1	1053.0
12-12-12-18	2226	2225.4	1990.0	1027.5
13-13-12-18	2204	2203.9	1928.9	1006.0
13-13-13-16	2174	2173.2	1932.6	1028.4
13-13-12-16		2228.0	1938.4	1031.5
12-13-12-16		2229.2	1969.0	1046.6
13-12-12-16		2243.2	1974.9	1037.0
12-13-13-16		2175.5	1962.0	1043.7
13-12-13-16	(2192)[b]	2192.3	1965.3	1034.0
12-12-13-16	(2195)[b]	2196.5	1991.5	1050.2

[a] Taken from C_3O_2, approximately the same as those derived by W. H. Smith and G. E. Leroi [*J. Chem. Phys.*, **45**, 1767 (1966)] (f_{Rr} and f_{rr} in their Table VI). [b] Observed but not definitely assignable to C_3O.

The assignment of this band to C_3O was made on the following basis. (1) The band grows readily with slight warming indicating that easily diffusing species are involved. Warming to a higher temperature is necessary to produce C_3O_2. (2) The molecule definitely contains CO and more than two carbon atoms. (3) The band grows in during both the conventional Knudsen-cell experiments where C_3 is present (as evidenced by a strong band at 2038 cm^{-1} for $^{12}C_3$) and in these "closed-cell" experiments where C_3 is undetectable. This indicates that the molecule is not C_4O since it would presumably form preferentially from the large amounts of C_3 and CO present in the Knudsen experiments.

A vibrational analysis of C_3O on the basis of the four observed frequencies in column 2 of Table I yields the stretching force constants given there and approximate predicted frequencies for the other two stretching modes. This analysis must be considered as tentative because of the meager experimental data. It can be seen from the calculated values of ν_3 in column 3 that the frequencies for the four unobserved mixed-isotope molecules essentially overlap the observed ones.

Bands for CCO (in argon) were observed here at 1969 ($^{12}C^{12}C^{16}O$), 1934 ($^{12}C^{12}C^{18}O$), and 1928, 1021 cm^{-1} ($^{13}C^{12}C^{18}O$). These four frequencies could be fit to within 2 cm^{-1} by the set of force constants, $f_{C-O} = 14.94$, $f_{C-C} = 6.02$, $f_{CC-CO} = 1.39$ mdyn/Å. They are not in complete agreement with those given by JMMT.[8]

Medium-intensity bands of $^{12}CN_2$ (in a N_2 matrix) were observed at 2858, 1253, and 394 cm^{-1}. These were shifted to 2836, 1232, and 392 cm^{-1} when ^{13}C was vaporized. They are in essential agreement with the earlier work.[5,9]

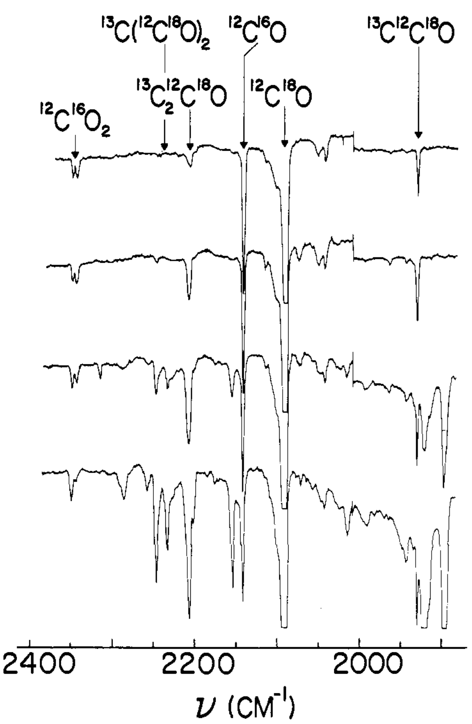

Figure 1. Infrared absorption spectra of an argon matrix at 4°K prepared by trapping ^{13}C atoms and $^{12}C^{18}O$. The top spectrum is of the original matrix at 4°K. Successive warming to about 20, 25, and 30°K, respectively, and quenching again to 4°K produced the changes shown in descending order. The arrow connected to $^{13}C(^{12}C^{18}O)_2$ indicates the center of a doublet appearing at 2228, 2243 cm^{-1}.

The corroboration of the C_2O and CN_2 frequencies is important because of the surprisingly different bonding in these isoelectronic molecules as indicated by the derived stretching force constants: $f_{CN} = 19.5$, $f_{NN} = 14.7$ mdyn/Å for CNN *vs.* $f_{CC} = 6.0$, $f_{CO} = 14.9$ mdyn/Å for CCO, or, crudely, C≡N=N *vs.* C—C≡O. There appears to be little possibility that the assignment is in error, so that the difference is a real one and is not readily explained by either the "doublet–quartet" approach[10] or the molecular orbital approach as applied by Purcell.[11]

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[8] We have reanalyzed the eight frequencies of JMMT[4] and find the force constants, $f_{C-O} = 14.82$, $f_{C-C} = 6.20$, and $f_{CO-CC} = 1.26$ mdyn/Å, in essential agreement with those derived here. The force constants in their Table VIII did not reproduce their frequencies.

[9] N. G. Moll and W. E. Thompson, *J. Chem. Phys.*, **44**, 2684 (1966).

[10] J. S. Shirk and G. C. Pimentel, *J. Amer. Chem. Soc.*, **90**, 3349 (1968).

[11] K. F. Purcell, *Inorg. Chim. Acta*, **3**, 540 (1969).

Chemisorption of Molecular Hydrogen on Zinc Oxide

Sir:

Two types of hydrogen chemisorption are evident on zinc oxide at room temperature:[1] type I is rapid and reversible; type II is slow (in part) and irreversible. Type II is unreactive in ethylene hydrogenation[1] and hydrogen–deuterium exchange[2] and its structure is unclear. Type I is the reactive species and ir studies suggest it forms Zn–H and O–H bonds by dissociation

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[1] A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, **73**, 3772 (1969).

[2] S. Naito, H. Shimizu, E. Hagiwara, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **67**, 1519 (1971).

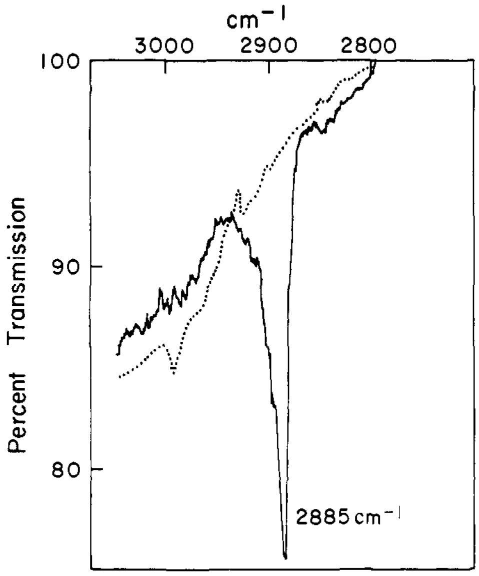

Figure 1. Spectrum of molecular deuterium on zinc oxide. The pressure and temperature are about 100 Torr and −195°, respectively. The spectrum was obtained on a 4× ordinate expansion mode. The dotted line shows the "background" for zinc oxide in the absence of deuterium.

on a limited number of zinc oxide pair sites.[1-3] Type I adsorption isotherms at room temperature approach saturation above 50 mm and studies of band intensities *vs.* pressure show similar effects. Moreover, when the sample in 50 mm of hydrogen is cooled to −195°, the band intensities change little. Since it has also been reported[2] that type II hydrogen chemisorption has a negligible rate at low temperatures, we would expect cooling in hydrogen above 50 mm from room temperature to −195° would result in no increase in adsorption beyond that attributable to physical adsorption. Taylor and Liang,[4] however, report that when zinc oxide is cooled in hydrogen at 1 atm from room temperature to −195°, there is an additional adsorption corresponding roughly to V_m for a nitrogen monolayer. Such extensive adsorption implies a heat of adsorption of several kilocalories, a value too great compared with the heat of liquefaction of hydrogen (0.216 kcal/mol[5]) to be ascribable to simple physical adsorption. Thus, it appears that there is a third type of chemisorption that is very weak and evident only at low temperature. Recently, Tamaru and coworkers[2] presented evidence that H_2-D_2 exchange may proceed *via* direct reaction of gaseous molecular hydrogen with type I hydrogen. Reaction *via* a weakly chemisorbed molecular hydrogen seems a more plausible alternative interpretation to us. Accordingly, it is tempting to assume that type III hydrogen adsorption may be this molecular species.

Figure 1 shows a band observed when zinc oxide at −195°[6] is exposed to deuterium. In addition to this band at 2885 cm⁻¹ bands also occur at 2584 and 1232 cm⁻¹ which are due to OD and ZnD species. The high frequency band arises from adsorbed molecular deuterium with the position shifted from that for gaseous deuterium,[7] 2990 cm⁻¹. This band, forbidden for the gas-phase ir, becomes allowed for the adsorbed species and the shift (105 cm⁻¹) is much larger than the shift typical for physically adsorbed species,[8,9] *i.e.*, about 20 cm⁻¹. Brief evacuation at −195° causes disappearance of this band, but the bands for type I chemisorption remain. Thus, the relatively weak adsorption responsible for the molecular band may, indeed, be the weak type III hydrogen chemisorption. Since the molecular band appears even when the type I sites are saturated, *i.e.*, on cooling in deuterium from room temperature, it is apparent that this molecular adsorption does not require empty type I sites. Bands ascribable to molecular species are also observed for adsorbed hydrogen and hydrogen deuteride at the expected positions; hence, it seems quite clear that we are dealing with a molecular species.

The spectral characteristics of the band for molecular adsorption on zinc oxide are quite different from those seen for physical adsorption on porous glass.[9] For example, the shift from the gas phase position is about five times that found with porous glass. Since, in simple interpretations,[10] solvent shifts are proportional to the interaction potential, the interaction potential for hydrogen with zinc oxide would be about five times that with porous glass provided the interaction distance is the same. Intensities, too, are markedly different; the extinction coefficient for hydrogen on zinc oxide is *at least* an order of magnitude greater than that reported for porous glass.[9] Reliable estimates must await more detailed studies, but our current best estimate suggests they differ by a factor of 65. Sheppard and Yates[9] related the extinction coefficient on porous glass to the "surface field" and thereby computed a surface field of 0.07 V/Å. If we followed the same procedure,[11] with our tentative extinction coefficient estimates, we would conclude that the surface field on zinc oxide is about 0.6 V/Å.

The foregoing shows that the nature of the adsorbed hydrogen (as gauged by ir) is highly specific to the adsorbent, zinc oxide, and, in that sense, is chemisorption.[12] We have also searched for molecular bands for nitrogen and oxygen adsorbed on zinc oxide at −195° but have failed to see such strongly shifted bands; hence, it appears that these surface sites are specific for hydrogen. We believe that this type of chemisorption may be common on certain dehydrated oxides. In particular, such chemisorption may be responsible for the low-temperature ortho–para conversion[13] and the chromatographic separation of

(3) R. P. Eischens, W. P. Pliskin, and M. J. D. Low, *J. Catal.*, **1**, 180 (1962).

(4) H. S. Taylor and S. C. Liang, *J. Amer. Chem. Soc.*, **69**, 1306 (1947).

(5) N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Sandusky, Ohio, 1952, p 129.

(6) This is the temperature measured at one point on the zinc oxide disk. Heating by the ir beam may occur inside the disk; hence, the mean temperature may be somewhat higher. Experimental procedures are those described by A. L. Dent and R. J. Kokes, *J. Amer. Chem. Soc.*, **92**, 6709 (1970).

(7) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1950, p 533.

(8) L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966, pp 296–308.

(9) N. Sheppard and D. J. C. Yates, *Proc. Roy. Soc., Ser. A*, **238**, 69 (1957).

(10) P. R. Monson, Jr., H. Chen, and G. E. Ewing, *J. Mol. Spectrosc.*, **25**, 501 (1968).

(11) Such estimates are probably not highly reliable inasmuch as they disregard changes in the polarity of the surface which contributes to the transition probability. See, for example, the discussion of solvent effects by A. D. Buckingham, *Proc. Roy. Soc., Ser. A*, **248**, 160 (1958).

(12) S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943, pp 27, 28.

hydrogen allotropes and isotopes by degassed alumina.[14] Indeed, the estimate of the surface field given above for zinc oxide is of the same order as estimates made by different techniques for adsorbed hydrogen on alumina.[14,15] Further studies aimed at more fully characterizing this weak hydrogen chemisorption are underway.

Acknowledgment. This work was aided by funds from the NSF under Grant No. GP-22830.

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(13) F. H. Van Cauwelaert and W. K. Hall, *Trans. Faraday Soc.*, **66**, 454 (1970).

(14) J. King and S. W. Benson, *J. Chem. Phys.*, **44**, 1007 (1966).

(15) F. H. Van Cauwelaert and W. K. Hall, presented at the Second North American Meeting of The Catalysis Society, Houston, Tex., Feb 24-26, 1971.

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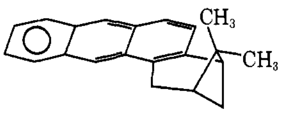
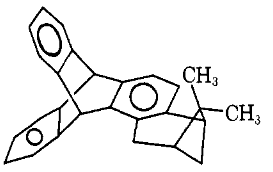
Anomalous Preferential Addition of Dienophiles to the Hindered Face of Apopinanthracene[1]

Sir:

Apopinanthracene[2] (ApAn) is an unusual aromatic hydrocarbon that does not have a symmetry plane by virtue of *gem*-dimethyl groups at C_3. Consequently it has two faces, β (front) and α (back), relative to the *gem*-dimethyl group.[3] Two sharp signals (40 and 88 Hz, 3 H each) are observed in the alkyl region which correspond to the *syn*- (shielded) and *anti*-C_3Me groups, respectively. In the corresponding triptycene, **1** (mp 223-225°, from ApAn and benzyne), both the *syn*- and *anti*-C_3Me resonances are shifted further upfield (to 30 and 79 Hz, respectively) as a result of increased shielding by the angular aromatic ring.



ApAn



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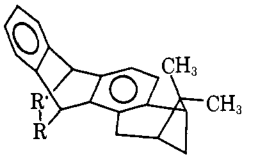
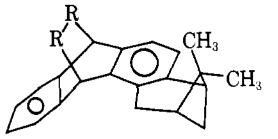
The reaction of ApAn with other dienophiles should in principle lead to two kinds of adducts as a result of frontside (β) and backside (α) attack. *A priori* backside attack (α) would be expected to predominate from steric considerations.

A mixture of Diels–Alder adducts, **2**, was prepared from ApAn and dimethyl acetylenedicarboxylate (DMAD). Pmr analysis, utilizing the relative area of the two *syn*-C_3Me signals at 29 (33%) and 36 Hz (67%), was used to determine the amount of each adduct. The signal at 29 Hz was assigned to **2**α, since the juxtaposition of the angular aromatic ring and the *syn*-C_3Me group in this isomer is almost identical with that in apopinotriptycene (**1**), and that at 36 Hz was assigned to **2**β. Unexpectedly, there is a preference by a factor of two (67:33) for [4 + 2] cycloaddition to the "wrong" (more hindered) side.



α



β

2(α, β), R–R = MeO_2CCCCO_2Me

3(α, β), R–R = $(NC)_2C$-$C(CN)_2$

4(α, β), R–R = *o*-F_4C_6<

5(α, β), R–R = O–O

Consequently, the reaction of ApAn with various dienophiles [tetracyanoethylene (TCNE), tetrafluorobenzyne (TFB), and singlet oxygen ($^1O_2$)] was undertaken in order to determine the generality of this phenomenon (Table I). The reaction products were analyzed by pmr and structural assignments were made in accordance with the aforementioned reasoning. In all cases the major isomer (60–70%) was formed by addition to the β (more hindered) face of ApAn.

Table I. Ratio of Diels–Alder Adducts from ApAn and Various Dienophiles

Dienophile	Adduct(s)[a]	Chemical shift, Hz (rel area) *syn*-C_3Me	*anti*-C_3Me	β/α addition
Benzyne[b]	**1**	30 (1)	78 (1)	
DMAD[c]	**2**α	29 (0.33)	80 (1)	2
	2β	36 (0.67)	81	
TCNE[c]	**3**α	29 (0.40)	86 (1)	1.5
	3β	43 (0.60)	87	
TFB[d]	**4**α	30 (0.35)	79 (0.38)	1.9
	4β	39 (0.65)	87 (0.62)	
$^1O_2$[e]	**5**α	28 (0.33)	80 (0.33)	2
	5β	40 (0.67)	82 (0.67)	

[a] Product composition independent of reaction conditions. [b] Generated from benzenediazonium 2-carboxylate in 1,2-dichloroethane. [c] Reaction effected in dioxane or carbon tetrachloride. [d] Generated from bromopentafluorobenzene and magnesium in THF. [e] Reaction effected in CS_2 using Rose Bengal as the sensitizer.

With maleic anhydride (MA), all four possible Diels–Alder adducts were obtained[4]—*syn*-**6**β (38 Hz), *anti*-**6**β (34 Hz), *syn*-**6**α (31 Hz), and *anti*-**6**α (28 Hz). The ratio of β to α attack, *i.e.*, (*syn*- + *anti*-**6**β)/(*syn*- + *anti*-**6**α) was ~1 instead of 2.

The lower β/α ratio (1:1) for the ApAn–MA reaction is probably a consequence of lower reactivity of

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(1) Taken in part from the Ph.D. Thesis of J. G. M., Case Western Reserve University, 1971.

(2) (–)-3,3-Dimethyl-2,4-methano-1,2,3,4-tetrahydrobenz[*a*]anthracene, mp 102–103°, $[\alpha]^{25}D$ –149° (*c* 2, EtOH); 93% optically pure. All new compounds (except for **5**, unstable) gave analyses consistent with assigned chemical composition. Complete physical, spectral, and optical characterization will be reported in the full paper.

(3) *Cf.* steroid nomenclature conventions.

(4) Based on the *syn*-C_3Me resonances. These assignments received further support from the results obtained by adding 1,3,5-trinitrobenzene (TNB) to a solution of *syn*- and *anti*-**6**α and -**6**β in CCl_4 or $DCCl_3$. All of the *syn*-C_3Me group signals are affected in the order *anti*-**6**α ~ *syn*-**6**α > *anti*-**6**β >>> *syn*-**6**β.[5] With the addition of incremental amounts of TNB the *syn*-C_3Me resonance of *syn*-**6**α coalesces with *anti*-**6**α (31 → 28 Hz). Further addition causes *anti*-**6**β to coalesce with this (34 → 28 Hz). The *syn*-C_3Me signal of *anti*-**6**α was essentially unaffected (ΔHz ~ 1.0). This phenomenon can be reversed by the addition of a better acceptor (*e.g.*, ApAn[6] or 2-*tert*-butylanthracene) than **6**.

(5) The magnitude of ΔHz is related to the ability of the TNB to "affect" the environment of the *syn*-C_3Me group.

(6) ApAn and TNB form a blood-red charge-transfer complex. TNB and **6** apparently do not.