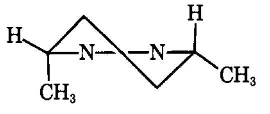
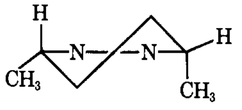
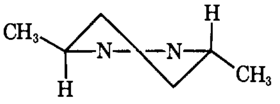

2a


2b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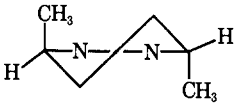
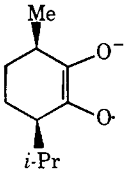

3b

greater than 1, the methine hydrogen splitting observed for $3\cdot^+$ would be nearly that expected for a pseudoaxial hydrogen, making the ratio of methine hydrogen splittings for $2\cdot^+/3\cdot^+ < 1$, since pseudoaxial hydrogens have a lower θ value and hence a larger splitting than pseudoaxial ones. Essentially this experiment has been done by Russell's group,[6] using the authentically flat semidione spin label, and giving the predicted result. The cis compound **4** showed the smaller splittings (10.8 and 6.7 for the two different α hydrogens). Since the conformations corresponding to **2a** and **2b** are not equal in energy, the splitting for the hydrogen on the carbon-bearing isopropyl is nearer the pseudoaxial value, and the other nearer the pseudoequatorial value. The trans compound **5** with both hydrogens almost exclusively pseudoaxial had $a(2\text{H}) = 12.4$. Since the hydrazinium cation radical label gave the reverse of this result, cis/trans splitting of about 2, the hydrazinium portion of the molecule is clearly not flat.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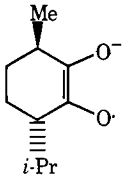
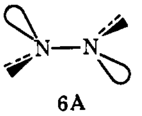
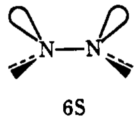

5

Deviation from planarity could occur in two basically different ways, to move toward an anti conformation (**6A**) or toward a syn one (**6S**). If the bending were toward **6A**, the prediction of the cis/trans methine splitting ratio being <1 would still hold, for the ring conformation would then be between a half-chair and a chair. Only if the hydrazine were bent toward the syn (**6S**) conformation would this ratio become >1. In this case, the ring would adopt a conformation tending toward a boat, and then the cis compound $2\cdot^+$ has the sterically more favorable conformations with C–H_β more nearly aligned with the spin-bearing orbitals on nitrogen ("bowsprit" type), while $3\cdot^+$ has pairs of conformations of equal energy which average the β hydrogens between favorable and unfavorable θ angles.[7]


6A


6S

Discussion of the amount of deformation from planarity and its consequences will occur in future publications.

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C_2O, CN_2, and C_3O Molecules[1]

Sir:

In the course of an investigation of the reactions of carbon atoms and molecules with each other at temperatures near 4°K,[2,3] a recurring infrared band appeared at 2244 cm^{-1}. It had also been observed by Jacox, *et al.* (JMMT),[4] when C_3O_2 was photolyzed in an argon matrix at 4°K. We report here the assignment of this band to the CCCO molecule formed by the trapping of carbon atoms with CO and their subsequent reaction to yield C_2O and then C_3O. CNN was prepared in a similiar way and the vibrational assignment of Milligan and Jacox[5] corroborated.

The furnace, variable-temperature dewar, and spectrometers used in the matrix-isolation experiments were similar to those described previously.[3] A beam of ^{12}C (or ^{13}C) atoms was vaporized from TaC[6] at temperatures near 3000°K by packing a thin-walled (0.008 in.) tantalum tube with graphite and allowing the carbon to essentially vaporize "through" the carbided tube.[3] ^{13}C was vaporized in the same way from 96% isotopically enriched graphite obtained from Mound Laboratory, Monsanto Chemical Co. At the highest temperatures some Ta atoms are also in the vapor and CO (from the graphite) is eliminated with difficulty. The carbon atoms were condensed with an argon: $^{12}\text{C}^{16}\text{O}$ mixture (200:1) onto a CsI window at 4°K. $^{12}\text{C}^{18}\text{O}$ was also used as a reactant (from Miles Laboratories, enriched to 92%). CNN was prepared by trapping carbon atoms in a pure N_2 matrix.

All isotopic combinations of the available C and CO were allowed to react, and the result for $^{13}\text{C} + {}^{12}\text{C}^{18}\text{O}$ is shown in the ir absorption spectra in Figure 1. The bands in the originally formed matrix are in the top tracing, and subsequent diffusions are shown in descending order. The CCO band at 1928 cm^{-1} is formed immediately, and the C_3O band (2204 cm^{-1}) and the doublet of C_3O_2 (2228, 2243 cm^{-1}) grow in with further warming and quenching. In the region of 1800–2000 cm^{-1} Ta(CO)_n bands also are formed[7] and unfortunately obscure the other, apparently weak, absorption band of C_3O expected in that frequency range. A stretching frequency for C_3O is also expected near 1000

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(1) The authors gratefully acknowledge the support of the Air Force Office of Scientific Research (NC-AFOSR 68-1588) and the National Science Foundation (GP-25411).

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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

$f_{C_1C_2} = 14.318$ $\quad f_{C_3O} = 16.548$ $\quad f_{C_1C_2-C_3O} = (1.29)^a$

$f_{C_2C_3} = 10.771$ $\quad f_{CC-CC} = (2.37)^a$

	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.

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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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