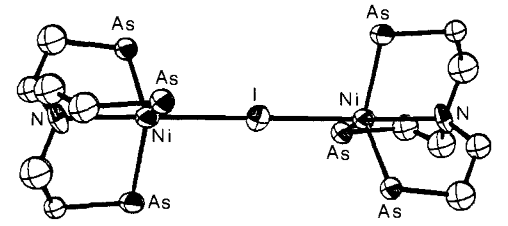

**Figure 1.** A schematic view of the skeleton of the $[Ni_2I(nas_3)_2]^+$ cation. The values of distances (Å) and angles (deg) are: Ni-I, 2.994 (3); Ni-N, 2.31 (2); Ni-As, 2.349 (5) (av); I-Ni-N, 178.0 (5); I-Ni-As, 95.2 (1) (av); As-Ni-As, 119.0 (2) (av).

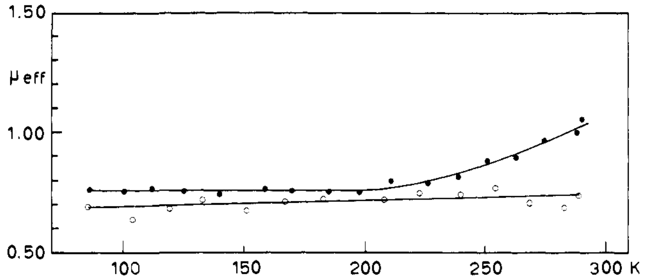

**Figure 2.** Variation with temperature of the magnetic moment $\mu_{eff}$ for Ni(I) in $[Ni_2Br(nas_3)_2]B(C_6H_5)_4$ (●) and in $[Ni_2I(nas_3)_2]B(C_6H_5)_4$ (○).

and $Z = 4$. The intensity data were collected on a Philips automatic diffractometer, with Mo K$\alpha$ radiation, using the limitation $6° \leq 2\theta \leq 20°$. The 1588 reflections having $I \geq 3\sigma(I)$ were considered observed and were used in the solution and refinement of the structure. The structure was solved by a Patterson synthesis followed by Fourier syntheses. The structure consists of dimeric $[Ni_2I(nas_3)_2]^+$ cations and $B(C_6H_5)_4^-$ anions with interposed tetrahydrofuran solvent molecules. Each nickel atom is bonded to the four donor atoms of the nas$_3$ ligand and to the shared bridging iodine atom. The iodine atom lies on a center of symmetry, while the boron atom of the $B(C_6H_5)_4^-$ ion is situated on a binary axis. The chromophore can be considered to be formed by two trigonal-bipyramids sharing a vertex. A schematic view of the $[Ni_2I(nas_3)_2]^+$ cation with the most significant bonds and angles is shown in Figure 1. The long axial distances Ni-I, 2.994 (4) Å, and Ni-N, 2.31 (2) Å, are noteworthy.

This complex is one of the few binuclear metal complexes having a linear metal-iodine-metal bridge.[4]

The magnetic behavior of these compounds has been studied over the range 84-290 K; in neither case is the susceptibility found to be field dependent. Diamagnetic corrections were calculated using Pascal's constants.[5] The $\mu_{eff}$ for each nickel atom vs. $T$ is reported in Figure 2. The iodo derivative has a $\mu_{eff}$ of ca. 0.7 BM in the temperature range of the measurements. The $\mu_{eff}$ of the bromo derivative has a constant value, 0.75 BM, from 84 to ca. 200 K; beyond this temperature the moment increases slowly up to the value of 1 BM at 288 K. The two complexes can therefore be considered essentially diamagnetic at low temperature, the residual value of $\mu_{eff}$ being attributable to paramagnetic impurities. In fact the magnetic susceptibility varies slightly from sample to sample but the plots obtained in each case are essentially the same as those in Figure 2 which shows the lowest $\mu_{eff}$ obtained.

This magnetic behavior suggests that an antiferromagnetic exchange takes place between the two nickel atoms involving the halide bridge. In terms of the Kramers-Anderson approach,[6] the antiferromagnetic coupling between the $d^9$ nickel cations can arise from the intermixing of a $d_{z^2}$ orbital on each nickel atom with a $P_z$ orbital on the bridging halide ion via the $P_\sigma$-$a_1'$ pathway.

The best pair of values of $g$ and $J$ for the bromo derivative, obtained fitting the Bleaney-Bowers equation to the experimental data by the use of a direct method to minimize the error-square sum over the observed susceptibilities,[7] is 2.00 and $-232$ cm$^{-1}$, respectively.

The increasing $\mu_{eff}$ value with temperature above 200 K for the bromo derivative is interpreted as due to the population of a thermally accessible triplet level. The fact that a different behavior is observed for the iodo derivative up to 290 K suggests that the exchange coupling between nickel atoms bridged by the iodine ion is greater than that in the bromide. This is in agreement with the general finding that the transfer integral and hence the exchange coupling constant $|J|$ becomes larger as the electronegativity of the anion decreases.

The diffuse reflectance spectrum of the bromo derivative shows a band at $1 \times 10^4$ cm$^{-1}$ and a shoulder at $1.31 \times 10^4$ cm$^{-1}$, while that of the iodo derivative has a band at $1.31 \times 10^4$ cm$^{-1}$. Both dimers show also intense bands above $1.8 \times 10^4$ cm$^{-1}$ attributable to charge transfer transitions. The shape and position of the first electronic absorption band are similar to those of typical five-coordinate nickel(I) complexes such as $[NiX(nas_3)]$[2] and also $[NiI(np_3)]$, which has been found, by X-ray analysis,[8] to have trigonal bipyramidal geometry. The similarity of the low energy bands is reasonable because the relatively weak spin-spin coupling in the dimers is expected to be small compared to the energies of the d-d transitions (ca. $1.1 \times 10^4$ cm$^{-1}$).

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*Received May 15, 1975*

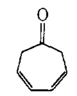
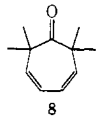
## Photochemistry of β,γ-Unsaturated Ketones. Specific Reactivity of $S_2$, $S_1$, and $T_1$ in 2,2,7,7-Tetramethyl-3,5-cycloheptadienone and Correlations with INDO Calculations[1]

*Sir:*

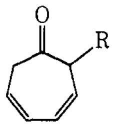
Direct irradiation at >300 nm of 3,5-cycloheptadienone (**1a**)[2-4] and the 2-methyl analog **1b**[2] gave only the hexatrienes **2** by decarbonylation of the lowest singlet excited state, while triplet sensitization of **1a** led only to the cyclobutene **3**,[3] i.e. $\Phi_{ST} = 0$.

The bridged ketone **4**, where the diene moiety is planar or near planar, gave decarbonylation and cyclobutene formation when irradiated at >300 nm, while triplet sensitization gave the [1,2]-sigmatropic acyl shift[5] (1,2-SAS) product **5**; again $\Phi_{ST} = 0$.[6] Similar reactions were reported for the trienone **6**[7] and the tropone-cyclopentadiene adduct **7**.[8,9]

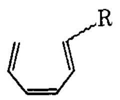
Table I. Calculated and Experimental Energies, Oscillator Strengths, and Configurational Compositions in Compounds Ia and 8

| | State | $E$, nm | | $f$ | | Composition, %$^b$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcd | Exptl | Calcd | Exptl$^a$ | $n,\pi_{CO}^*$ | $n,\psi_3$ | $\psi_1,\pi_{CO}^*$ | $\psi_1,\psi_3$ | $\psi_1,\psi_4$ | $\psi_2,\psi_3$ | $\psi_2,\psi_4$ |
|  1a | $S_1$ | 294 | 278–290$^c$ | 0.0024 | | 83 | 10 | 5 | | | | |
| | $S_2$ | 229 | 204–225$^c$ | 0.32 | | | | | | | 95 | |
| | $S_3$ | 207 | | 0.058 | | | 63 | | 13 | | | 17 |
| | $T_1$ | 478 | 539$^d$ | | | | | | | 15 | 78 | |
| | $T_2$ | 403 | | | | | 13 | | 32 | | | 52 |
| | $T_3$ | 326 | | | | 84 | 7 | 5 | | | | |
| | $T_4$ | 208 | | | | | 57 | | 6 | | | 31 |
|  8 | $S_1$ | 291 | 290$^e$ | 0.0015 | 0.0068 | 80 | 7 | 10 | | | | |
| | $S_2$ | 237 | 243$^e$ | 0.31 | 0.10 | | | | | | 95 | |
| | $S_3$ | 220 | | 0.090 | | | 66 | | 16 | | | 13 |
| | $T_1$ | 503 | 572$^e$ | | | | | | | 15 | 77 | |
| | $T_2$ | 437 | | | | | 17 | | 34 | | | 46 |
| | $T_3$ | 321 | | | | 81 | | 10 | | | | |
| | $T_4$ | 220 | | | | | 58 | | | | | 35 |

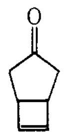
$^a$ Reference 25. $^b$ Only those configurations contributing more than 5% to a state are shown. $^c$ In 95% ethanol, ref 4, 26. $^d$ Reference 3. $^e$ In methanol, see also ref 10.



1a, R = H
b, R = Me



2



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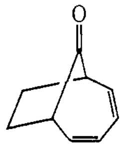

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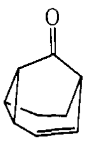

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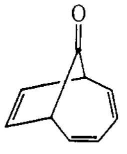

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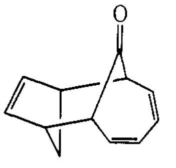

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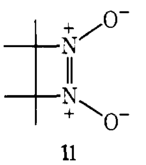


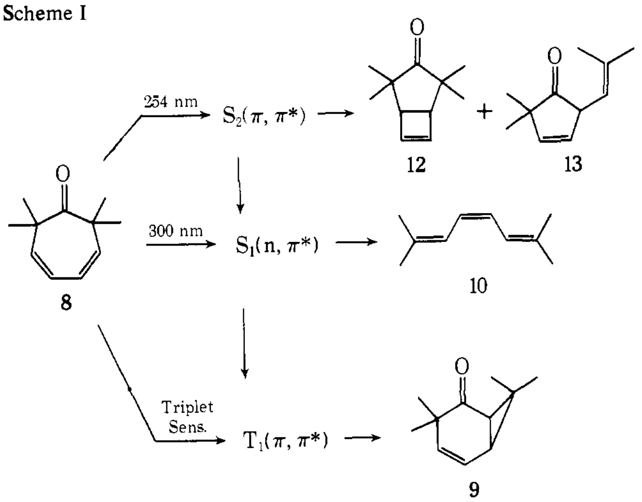
11

For all the 3,5-cycloheptadienones above a major singlet-derived reaction is decarbonylation. In contrast Paquette et al.[10] reported that 2,2,7,7-tetramethyl-3,5-cycloheptadienone (**8**) gave only one major photoproduct, the 1,2-SAS product **9**, on both direct and triplet sensitized photolysis, indicating that $\Phi_{ST} > 0$ in this case, although formation of **9** could not be quenched by naphthalene or piperylene.[10] However, we now report results in sharp disagreement with the earlier work[10] which indicate that the photochemistry of **8** is more diverse and indeed more interesting than previously indicated.

Irradiation of **8** at 300 nm through Pyrex in a variety of solvents (ethers, alcohols, hydrocarbons) gives in about equal yield *two* major products: the decarbonylation product, 2,7-dimethyl-2,4,6-octatriene (**10**) in addition to the 1,2-SAS product **9**. The identification of **10** is made from its spectral properties,[11] by comparison with an authentic sample,[12] and by an independent synthesis using the Wittig reaction of 2-butenedial[13] and 2 equiv of isopropyltriphenylphosphonium iodide.[14] Triplet sensitization of **8** using acetone or benzophenone gives only **9**, in agreement with the earlier report.[10] Formation of **9**, but not **10**, is quenched inefficiently by 1,3-cyclohexadiene ($E_T$ = 52–53 kcal/mol, $k_q\tau \sim 0.1\ M^{-1}$) and more efficiently by the low energy triplet quencher **11**[15] ($E_T$ = 35–42 kcal/mol, $k_q\tau = 38.5\ M^{-1}$ in $CHCl_3$, 29.5 $M^{-1}$ in $CH_3CN$), suggesting a very low triplet energy for **8** ($E_T \sim$ 45–53 kcal/mol) and a triplet lifetime of <10 nsec. Irradiation of **8** in $CCl_4$ gives only **9**, presumably due to enhanced ISC by external spin-orbit coupling in this heavy-atom solvent.

Irradiation of **8** at 254 nm through quartz gives *four* major and four minor unidentified products. The four major products were isolated by column chromatography, purified by preparative GLPC, and identified as **9**, **10**, 2,2,4,4-tetramethylbicyclo[3.2.0]hept-6-en-3-one (**12**),[16] and 2,2-dimethyl-5-(1-isobutenyl)-3-cyclopentenone (**13**).[17] Formation of cyclobutene **12** and (for the first time in 3,5-cycloheptadienone photochemistry) the 1,3-SAS product **13** is particularly interesting since they are formed only upon irradiation into $S_2$; it appears therefore, that *reaction from* $S_2$ *can compete with internal conversion (IC) from* $S_2$ *to* $S_1$ *or* $S_0$.

Scheme I



The photochemistry of **8** can be summarized as in Scheme I.

With the object of attaining a more detailed description of the excited states in **1a** and **8**, we have carried out molecular orbital calculations using an INDO model,[18] reparameterized[19] for the prediction of Franck-Condon maxima and singlet-triplet energy splittings, especially for n → π* transitions. The geometries of **1a** and **8** used in the calculations were found from carefully chosen bond distances and angles,[22] the molecules being confined to $C_2$ symmetry with a diene dihedral angle of 51.2°. Due to the $C_2$ symmetry, the molecular orbitals show large contributions from many atoms and several orbitals from each atom, but it is nonetheless possible to identify molecular orbitals which are mainly localized in the carbonyl group ($n_{CO}$ and $\pi_{CO}$) or on the diene moiety ($\psi_1 \ldots \psi_4$). Examination of the ground state charge-density matrices shows no significant disturbance of the charge distribution in the ring due to the presence of the methyl groups in **8** compared to **1a**, neither in the overall charge or its $\sigma$ and $\pi$ components, the changes being of the order of 0.02 electrons.

Excited state calculations were then performed in the singly excited configuration-interaction approximation[23] with inclusion of a large number (~70) of configurations to obtain the excited state energies and oscillator strengths for the singlets in the dipole length approximation, including one-center sp terms,[24] consistent with the INDO model. The results on **1a** and **8** are shown in Table I.

The calculated states and their energies are in good agreement with observed spectroscopic properties, the estimate of $E_T$ from the quenching experiments on **8**, and the commonly accepted singlet-triplet energy splittings for $n \rightarrow \pi^*$ transitions (0.4 eV).[27] Some results from CNDO/S calculations on **1a** and **8** have recently been published by Houk et al.[9,28] Although details about the calculations and results were not given, some of their results and conclusions are in apparent disagreement with our present calculations and need reinterpretation. It was stated[9] that $T_1$ was $\pi,\pi^*$ for **1a** and $n,\pi^*$ (or CT) for **8**, and that the relative energies of the states of these systems were "extremely sensitive" to symmetry and substituents. The calculations[9] were used to explain apparent variations in singlet and triplet photochemistry as well as intersystem crossing efficiencies in 3,5-cycloheptadienones, in agreement with the reported[10] photochemistry of **8**, which we now have shown to be largely incorrect, especially with respect to singlet reactivity. In contrast, our calculations show a striking similarity in both the energies and contributions of configurations of all low-lying singlet and triplet states of **1a** and **8**.

Our calculations are useful in interpreting the observed photochemistry of **8**. In $S_1$ the excitation is largely localized on the CO group, and we find expulsion of CO is the dominant if not the exclusive reaction mode. In $S_2$ the excitation is largely localized in the diene, and cyclobutene formation is observed. We had previously concluded[6] that cyclobutene formation from the singlet manifold occurs only from planar dienones such as **4**, **6** and **7**. In the case of **8**, it is conceivable that the $S_2$ state relaxes from a twisted ($C_2$) toward a planar ($C_S$) diene conformation, allowing disrotatory ring closure to compete efficiently with IC. We can examine this hypothesis through additional calculations on geometrically altered dienones. Furthermore, the similarity in the state diagram for **1a** and **8** suggests that the rate constants for ISC should be nearly identical for the two compounds. Differences in $\Phi_{ST}$ must therefore be attributable to structural effects on competitive reactions from $S_1$, in particular on the rate of decarbonylation. We are now determining these rate constants explicitly using fluorescence lifetime measurements.[29]

The striking similarities in the results of our theoretical calculations on **1a** and **8** suggest that wavelength dependent photochemistry should be observed for **1a** and probably other 3,5-cycloheptadienones and perhaps as a general feature of the photochemistry of $\beta,\gamma$-unsaturated ketones. We intend to explore this possibility.

**Acknowledgments.** We thank Professor M. Goldstein of the ERDA Courant Computation Center for a generous grant of computer time. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research through a grant to M.A.R.

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(11) Spectral properties of **10**: NMR $\delta_{TMS}$ ($CCl_4$) 1.76 (br s, 12 H, methyls), 5.6–6.3 (complex m, 4 H, vinyls); uv $\lambda_{max}$ ($CH_3OH$) 292 ($\epsilon$ 38,600), 280 ($\epsilon$ 55,000), 269 nm ($\epsilon$ 38,600); ir $\nu$ ($CCl_4$) 3040, 2970, 2920, 2860, 1640, 1380, 1000, 960 $cm^{-1}$, no $\nu_{CO}$.

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(16) Spectral properties of **12**: NMR $\delta_{TMS}$ ($CCl_4$) 1.02 (s, 6 H, methyls), 1.10 (s, 6 H, methyls), 3.16 (s, 2 H, methynes), 6.25 (s, 2 H, vinyls); $\nu_{CO}$ 1725 $cm^{-1}$.

(17) Spectral properties of **13**: NMR $\delta_{TMS}$ ($CCl_4$) 1.07 (s, 6 H, methyls), 1.75 (br s, 6 H, methyls), 3.70 (br d, 1 H, $\alpha$H), 4.80 (br d, 1 H, exocyclic vinyl), 5.92 (br s, 2 H, vinyls); $\nu_{CO}$ 1740 $cm^{-1}$.

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## Solvation of Gaseous Carbanions in Dimethyl Sulfoxide [1]

*Sir:*

We present here solvation energies for several classes of carbanions which are of importance to synthetic and theoretical organic chemistry. The effect of structural variation on their solvation energies can be understood roughly in terms of charge delocalization and steric hindrance to solvation.