9. Electronic and Molecular Structure of the $C_8H_{10}^{+\cdot}$ Valence Isomers 1,3,5-Cyclooctatriene$^{+\cdot}$ and Bicyclo[4.2.0]octa-2,4-diene$^{+\cdot}$ from their Electronic Absorption Spectra in *Freon* Glasses

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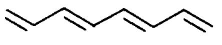
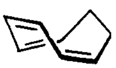
The molecular cations of 1,3,5-cyclooctatriene (COT$^{+\cdot}$) and bicyclo[4.2.0]octa-2,4-diene (BCO$^{+\cdot}$) can be observed intact in γ-irradiated *Freon* glasses, as opposed to Ar matrices where ionization is accompanied by extensive rearrangements. This proves the superiority of the *Freon*-glass method for the generation of metastable primary cations. The electronic absorption (EA) spectra reveal *a)* that a previous analysis of the BCO$^{+\cdot}$ electronic structure on the basis of the ultraviolet photoelectron (UP) spectrum of BCO was incomplete, and *b)* that COT undergoes planarization upon ionization, in accord with qualitative expectations and MNDO calculations. A previously proposed LCBO model was used to assess the influence of the above geometry change on the electronic structure of COT$^{+\cdot}$.

Introduction. – The pair of C_8H_{10} valence isomers, 1,3,5-cyclooctatriene (COT) and bicyclo[4.2.0]octa-2,4-diene (BCO) have received repeated attention since *Cope et al.* first suspected [1] and later confirmed [2] that all syntheses of COT [3] actually led to an equilibrium mixture of COT and BCO1).



OTE



COT

BCO

Subsequently, methods of separation [2] [3c] [5] or independent synthesis of BCO [6] were developed, and the thermochemistry of the COT⇆BCO equilibrium was assessed in solution [7] and later also in the gas phase [8]. Concurrently, the solution photochemistry of COT [9] and BCO [5] was explored and revealed interesting novel transformations, among them the photoinduced ring opening of BCO to COT [5]. This reaction, which is orbital-symmetry-forbidden along the (sterically enforced) disrotatory pathway [10], was later shown to proceed *via* (*Z,Z*)-octatetraene detected as a transient upon flash photolysis [11] or as a primary photoproduct of BCO in an Ar matrix [12].

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1) According to the observations and data reported by *Willstätter* and *Waser* [4], rather pure COT may have been obtained in their first attempt to synthesize this compound. Note also that independent from *Cope* and *Hochstein* [1], *Ziegler* and *Wilms* [3b] carefully separated the products obtained by reduction of cyclooctatetraene with Na and found COT and bicyclo[4.2.0]octadiene to which they erroneously assigned the 3,6-diene structure.

In 1972, the ultraviolet PE (UP) spectrum of COT was measured by *Heilbronner* and coworkers and interpreted in terms of a nonplanar geometry with twist angles of 53° between adjacent double bonds [13], a prediction which later received support from a force-field calculation [14]. The UP spectrum of BCO was published later by *Gleiter et al.* who used a group orbital model to construct an MO scheme of BCO in accord with their experimental findings [15].

Recently, the radical cations of linear conjugated polyenes [16] [17] and their (poly)cyclic valence isomers, have been studied. In particular, the electronic absorption (EA) spectra of ionized COT [18] [19] and BCO [19] were obtained in Ar matrices. They were of very complex but similar appearance, and indicated that both species undergo extensive rearrangement upon ionization in this medium. Upon selective photolyses, both spectra could be converted to those of 1,3,5,7-octatetraene$^{+\cdot}$ (OTE$^{+\cdot}$) in different conformations [17].

Since the spectra of COT$^{+\cdot}$ and BCO$^{+\cdot}$ could not be distinguished in Ar matrices [19], we turned to *Freon* glasses [20] which are generally better suited for the observation of metastable *primary* cations. Ionization of the title hydrocarbons in this medium did indeed result in very simple and clearly distinguishable spectra which could be readily assigned in terms of the parent cations. The purpose of this paper is to describe these results and propose an interpretation thereof which leads to a partial reassignment of the UP spectrum of BCO. Apart from this, we found that the photochemistry of BCO$^{+\cdot}$ takes an entirely different course in *Freon* glasses where a cation complex between benzene and ethylene is formed instead of OTE$^{+\cdot}$, the dominant photoproduct in Ar matrices [21].

Materials. – An equilibrium mixture of COT and BCO was obtained by reduction of cyclooctatetraene with Zn in KOH/EtOH [22]. The major (85%) component was separated by prep. GC to yield COT of > 99% purity (^{2}H-NMR). This method was, however, too tedious for the isolation of sufficient BCO (present in five times smaller quantities). On the other hand, the method of *Roth* and *Peltzer* [5] which consists of the continuous removal of BCO from the COT$\leftrightharpoons$BCO equilibrium by slow distillation over a suitable temp. gradient is only applicable, if sufficient quantities of material are available to saturate the required 1.5-m spinning band column. Therefore, a direct synthetic approach was chosen which takes advantage of the observation [23] that, upon heating, the $Fe(CO)_3$ complex of COT is quantitatively transformed into that of BCO. Subsequent oxidation of the purified BCO complex with Ce(IV) in acetone at 0° liberated BCO which was free of COT according to ^{1}H-NMR. Due to problems during workup (see *Experimental Part*), up to 10% BCO were reconverted to COT by the time the hydrocarbon was completely separated from solvents, so that the BCO samples employed in the experiments described below still had to be purified by prep. GC. Nevertheless, we believe that the Fe complex route is best suited for the preparation of gram quantities of BCO.

Results. – *Fig. 1* shows the EA spectra of 5×10^{-3} M frozen solutions of COT and of BCO in $CFCl_3/CF_2BrCF_2Br$ [24] exposed to ~ 0.5 Mrad γ-radiation. They are drawn to scale beneath the UP spectra of COT and BCO (top traces) which were remeasured for a precise determination of I_a^1. The latter agree essentially with those published earlier [13] [15], but we note already at this point that the area under the second band system in the BCO spectrum is roughly *four* times as large as that under the first band, suggesting that the former comprises four ionization events in contrast to the previous interpretation [15] which had assigned only *three* BCO MO's to this energy region.

It is immediately evident that the EA spectra differ substantially from those obtained earlier in Ar matrices [19] in that they show much fewer spectral components. In particular, neither spectrum shows any trace of OTE$^{+\cdot}$, which can clearly be distinguished by its sharp peaks in the 500–440-nm range [17]. Since OTE$^{+\cdot}$ is the major product observed

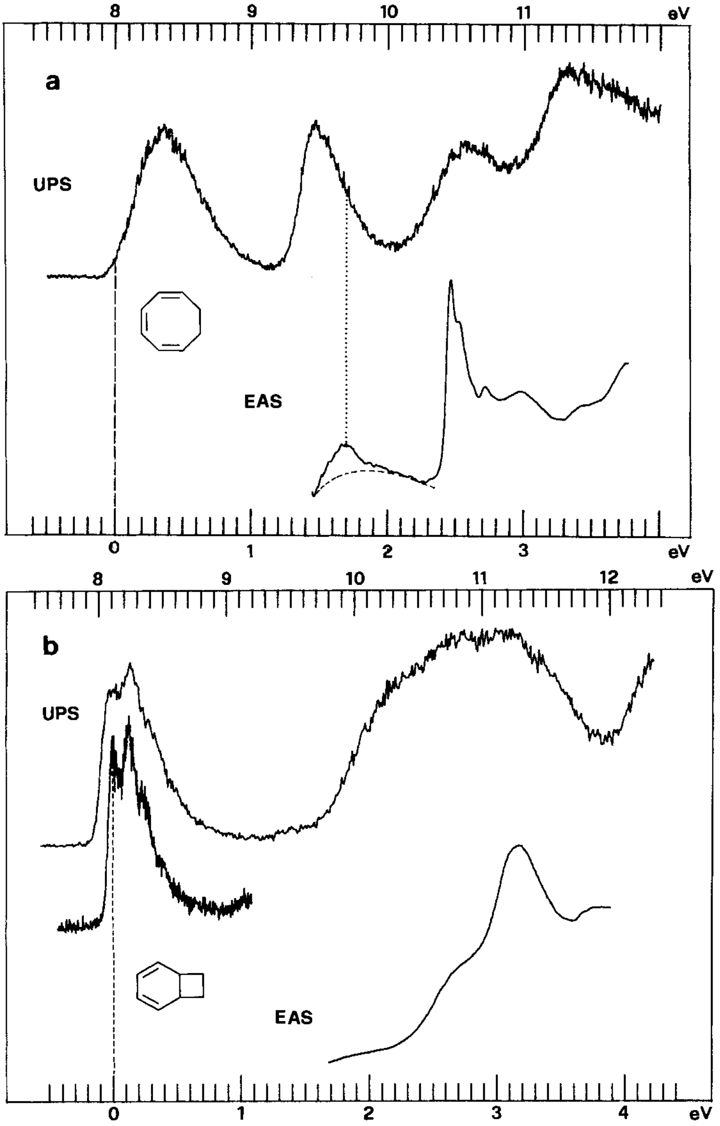

Fig. 1. *EA Spectra of ionized 1,3,5-cyclooctatriene (COT,* a*) and bicyclo[4.2.0]octa-2,4-diene (BCO,* b*) drawn to scale under the UP spectra of the corresponding neutrals.* The inset under the first UP band of BCO shows a partial high resolution (18 meV *fwhm*) scan for a more precise determination of I^1_{V}.

after ionization of both COT and BCO in Ar matrices, we conclude that no rearrangements occur in the *Freon* glass, and that the spectra in *Fig. 1* are those of the parent cations.

Discussion. – *The Electronic Structure of BCO*$^{+\cdot}$. In a first approximation, we expect the EA spectrum of $BCO^{+\cdot}$ to show the general features of a diene cation spectrum [16], *i.e.* a weak low-energy and a more intense high-energy transition which is indeed what is observed. Moreover, the BCO$^{+\cdot}$ spectrum (λ_{max} = 490 and 405 nm) is very similar in appearance and band position to that of the cyclohexadiene radical cation (CHD$^{+\cdot}$, λ_{max} = 474 and 388 nm [25]) in the same medium. Assuming a minimal perturbation of the diene chromophore by the cyclobutane moiety (a proposition which will be examined in more detail below), the first excited state at 2.5 eV can be approximately described by a diene (π_1^{-1}) hole configuration2). Ionization from π_1 should, therefore, occur at

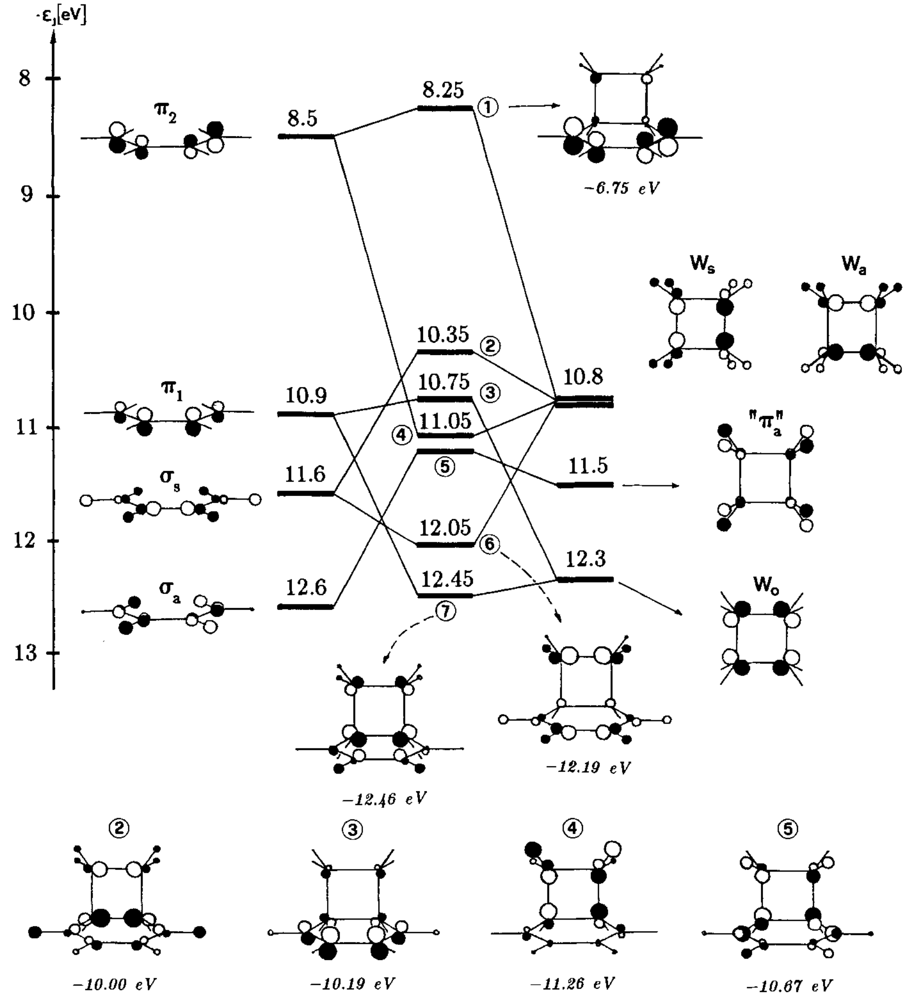

Fig. 2. *MO Diagram illustrating the interaction of an s-*cis*-butadiene and a cyclobutane moiety.* Bold numbers are empirically derived BCO orbital energies (see text). All MO plots are based on STO-3G wave functions at MNDO optimized geometries (STO-3G orbital energies in *italics*).

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2) As discussed in [16], configuration interaction (CI) plays an important role in the description of polyene$^{+\cdot}$ excited states. For the sake of a simple MO model, we will assume that the leading configurations offer a useful description of BCO$^{+\cdot}$ excited states. For a diene$^{+\cdot}$, this is a less fallacious approximation than for cations of longer polyenes.

(8.25 + 2.5) = 10.75 eV, *i.e.* within the broad second UP band of BCO. However, in a recent discussion of the $BCO^{+\cdot}$ electronic structure [15], this MO was not considered, which led us to reinvestigate the group orbital interaction scheme.

The result is displayed in *Fig. 2* which shows an orbital-interaction diagram for the cyclobutane and the s-*cis*-butadiene fragments including the σ-MO's of the latter.

Assuming that the inductive influence of the cyclobutane moiety leads to a raising of the s-*cis*-diene orbitals by ~ 0.6 eV [15] [26] and that the inverse effect on the cyclobutane MO's is 0.2 eV [26], we arrive at empirically derived basis energies of 8.5 (π_2), 10.9 (π_1), 11.6 (σ_s), and 12.6 (σ_a) eV for butadiene as well as 10.8 (antisymmetric and symmetric *Walsh* orbitals W_a/W_s), 11.5 (pseudo π orbital 'π_a'), and 12.3 ('outer' *Walsh* orbital W_o) for cyclobutane.

According to the observed $I^1_v = 8.25$ eV, π_1 is raised through interaction with W_a by 0.2 eV[3]) *(level 1)* while W_a is concomitantly lowered to 11.05 eV *(level 4)*. The interactions between the remaining fragment MO's cannot be readily extracted from the PE spectrum and will, hence, be discussed on the basis of model considerations. If the matrix element for the $\pi_1 - W_o$ interaction is taken to be –0.5 eV[4]), the resulting MO's will lie at –10.75 eV *(level 3)* and –12.45 eV *(level 7)*. Furthermore, W_s of cyclobutane is well disposed to mix with σ_s of BD to yield an out-of-phase combination *(level 2)* which we assign to the shoulder at 10.35 eV in the second PE band of BCO and a positive combination which would, therefore, lie at ~ 12.05 eV *(level 6)*. Finally, 'π_a' of cyclobutane will be raised through interaction with σ_a of butadiene and lie also within the second PE band *(level 5)*.

The above results are conveniently illustrated by the MO plots in *Fig. 2* which reflect the above derived mixing patterns. Incidentally, the orbital sequence predicted by STO-3G is the same as that emerging from the above PMO considerations with the exception of MO's ④ and ⑤ which are inverted.

Most importantly, the above analysis predicts at 2.5 eV gap between π_1 and π_2 of BOD, *i.e.* the two MO's involved in the electron promotion giving rise to the first EA band of $BCO^{+\cdot}$, in good agreement with experiment. Furthermore, it shows that the second PE band of BOD contains *four* ionization processes (including ionization from $\pi_1 - W_o$ which had escaped notice in an earlier analysis of the $BCO^{+\cdot}$ electronic structure on the basis of the PE spectrum alone [15]). Finally, inspection of the wave functions in *Fig. 2* shows that among the excitations within the occupied manifold of MO's, only that from $\pi_1 - W_o$ *(level 3)* to $\pi_2 - W_a$ *(level 1)* will give rise to a sizeable transition moment because of poor overlap of all other wave functions with the latter.

With regard to the second, more intense band of $BCO^{+\cdot}$, we note that it is almost exactly at the same energy as in cyclohexadiene$^{+\cdot}$ ($CHD^{+\cdot}$), both being, however, red-shifted relative to parent 1,3-butadiene cation ($BD^{+\cdot}$ [17]) by 0.85 eV. This shift is reminiscent of that between λ_{max} of the corresponding neutrals ($\lambda_{max}(BD) = 217$ nm; $\lambda_{max}(BCO) \approx \lambda_{max}(CHD) = 260$ nm [28]; difference = 0.93 eV) which reflects the similarity of the electronic transitions in the neutrals and the cations, both corresponding essentially to HOMO → LUMO excitation. Thus, we conclude that the antibonding pseudo-π

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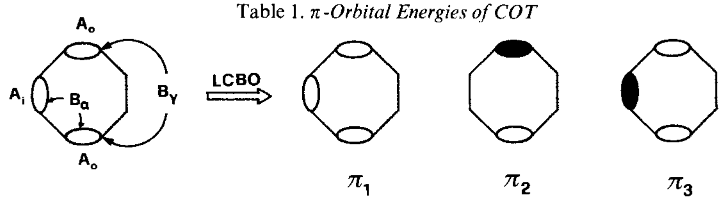
[3]) From this raising and the MO coefficients at the interacting centers, the resonance integral β for $p(\pi) - p(W)$ interaction ($p(W)$ being the contribution of the cyclobutane W_a HOMO at the sites of interaction with the butadiene moiety) can be deduced. Thus, we obtain $\beta = -1.33$ eV, a value which is substantially lower than that proposed earlier for a similar $p(\pi) - p(W)$ interaction in isomeric bicyclo[4.1.1]octa-2,4-diene [27]. As pointed out in [15], this may be due to the ~ 30° tilting of the p(W) relative to the $p(\pi)$ AO's in the present case of BCO (*cf.* angle between the six-membered and the four-membered ring). This effect is probably reinforced by the hybridization of the p(W) AO's along the C–C bonds (see *Fig. 2*).

[4]) $\langle \pi_1|H|W_o\rangle = 2 \times 0.5 \times 0.372 \times \langle p(\pi)|H|p(W)\rangle$. The latter parameter $\beta(\pi/W)$ is equal to –1.9 eV, if $p(\pi)$ and p(W) are pure p-AO's in a parallel arrangement [27]. Here, they are twisted by 45° which brings $\beta(\pi/W)$ down to $-1.9 \text{ eV} \times \cos(45°) = -1.34$ eV.

orbitals of the CH_2CH_2 bridge in CHD seem to serve equally well for lowering the energy of π_3^* as the (presumably lower-lying) antibonding *Walsh*-MO's of cyclobutane in the case of BCO.

Electronic Structure of $COT^{+\cdot}$. The spectrum of COT^{+} shows the expected triene cation features [16], *i.e.* a weak first band ($\lambda_{max} \approx 710$ nm, 1.75 eV) superimposed on a weak matrix background absorption (broken line) and an intense second band ($\lambda_{max} = 505$ nm, 2.45 eV), both absorptions being strongly shifted from their positions in open-chain triene cations. As in the previous case of BCO^{+}, we will try to relate the molecular ion's EA spectrum to the UP spectrum of the neutral. This has been analyzed by *Heilbronner et al.* [13] within the framework of a linear combination of bond orbitals model (LCBO, see the scheme above *Table 1*).

Table 1. *π-Orbital Energies of COT*



Method		$-\varepsilon(\pi_1)$	$-\varepsilon(\pi_2)$	$-\varepsilon(\pi_3)$	$-\varepsilon(\pi_4^*)$
PES	($\theta = 53°$)	10.61	9.48	8.37	–
LCBO	($\theta = 53°$)	10.66	9.49	8.38	–
LCBO	($\theta = 0°$)	11.41	9.42	7.69	–
Δ(LCBO)		−0.75	+0.07	+0.69	–
MNDO	($\theta = 49°$)	10.95	10.04	8.97	0.13
MNDO	($\theta \approx 0°$)	11.65	10.04	8.23	−0.60
Δ(MNDO)		−0.70	± 0.00	+0.74	−0.63

From the mean of the three observed vertical π IP's (8.37, 9.48, and 10.61 eV, see *Fig. 1, a*) they deduced basis energies of $A_i = -9.68$ and $A_o = -9.41$ eV for the inner and outer π bonds, respectively. Given those off diagonal matrix elements, $B_\alpha = -0.8$ eV for 1–2 and $B_\gamma = -0.06$ eV for 1–3 interactions between double bonds optimally reproduced the above experimental figures (see first two rows of *Table 1*). From $B_\alpha = -1.31$ eV for coplanar conjugated double bonds and $B_\alpha(\theta) = B_\alpha(0°)\cdot\cos\theta$, they deduced a dihedral angle of $\theta = 53°$ between adjacent π bonds, a prediction which later received support through a force-field calculation giving $\theta = 51°$ and 54° [14][5]).

From the UP spectrum of COT, we would predict λ_{max} for the first EA band of COT^{+} at $I_v^2 - I_a^1 = 1.48$ eV[6]) corresponding to 837 nm, a figure which is not accord with the observed $\lambda_{max} \approx 710$ nm. Such disagreements are usually indicative of pronounced geometry changes upon ionization such as they are actually suggested by the broad envelope of the first UP band of COT. In fact, the increase in the 2–3 and 4–5 π bond orders upon

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[5]) Note that due to a twisting of the CH_2CH_2 bridge, COT has no plane of symmetry and, therefore, the two 'terminal' double bonds (and the angles they form with the central double bond) are inequivalent.

[6]) We have to take the *adiabatic* ionization potential as a reference energy, because we observe the EA spectrum of the cation in its *equilibrium* geometry. From the UP spectrum in *Fig. 1*, we obtain $I_a^1 = 8.0$ eV.

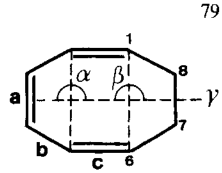

Table 2. *Results of Semimepirical Calculations on COT and COT*$^{+}$ [a])

Compound	(Method)	a	b	c	α	β	γ[b])	ΔH_f°
COT	(MINDO/3)	135.1	145.9	134.8	178.4	178.3	60.3	120.0
COT	(MNDO)	135.0	146.3	134.8	145.2	146.0	63.6	142.0
$COT^{+\cdot}$	(MINDO/3)	141.0	141.0	138.7	179.9	179.8	62.9	848.5
COT^{+}	(MNDO)	141.5	141.2	139.6	179.5	179.0	46.4	909.0

[a]) Bond lengths in pm, angles in degrees, energies in kJ/mol.

[b]) Angle between the 1–6 and the 7–8 connecting lines viewed along their midpoints (twist angle of the CH_2CH_2 bridge).

ionization will constitute a driving force for planarization of the molecular cation, similar to the cases of biphenyl [29] or styrene [30]. To test this qualitative prediction, we performed some semiempirical structure calculations whose results are collected in *Table 2*.

Unfortunately, MINDO/3 predicts the π system to be essentially planar already in neutral COT ($\alpha = \beta \approx 180°$, hence $\theta \approx 0°$), but MNDO which gives a more realistic equilibrium geometry of the neutral ($\theta = 49°$, in good agreement with the above mentioned predictions) clearly shows that ionization results in planarization of COT with θ nearly 0° (accompanied by some distortion of the 'terminal' double bonds due to the influence of the twisted CH_2CH_2 bridge).

If we assume that the π bond basis energies remain constant, we can readily assess the influence of this geometry change on the electronic structure of COT^{+} within the LCBO model of *Heilbronner et al.* [13]. Taking $B_\alpha = -1.31$ eV for the now coplanar π bonds and setting $B_\gamma = 0$[7]), yields $-\varepsilon(\pi) = 7.69$, 9.42, and 11.41 eV for hypothetical planar COT (see *Table 1*). Apparently, planarization has very little effect on the position of π_2[8]), while the HOMO (π_3) is destabilized and π_1 is stabilized by ≈ 0.7 eV. The latter numbers are reproduced amazingly well by MNDO (last line in *Table 1*). With respect to the first EA band of $COT^{+\cdot}$, this implies λ_{max} at $9.42-7.69 = 1.73$ eV corresponding to 717 nm, in much better agreement with the observed $\lambda_{max} \approx 710$ nm (*Fig. 1, b*). Conversely, we can deduce from the same model that $\theta \approx 0°$ for the molecular cation.

Turning to the second EA band of $COT^{+\cdot}$, we note that it coincides rather well with the third PE band of COT. Although the state observed in the EA spectrum (leading configuration = HOMO→LUMO excitation, *cf.* $^2B_g^+$ in hexatriene cation [16]) should contribute to the photoionization cross section in proportion to the admixture of the (π_2^{-1}) excited *Koopmans'* configuration, it is the state arising from π_1 ionization which dominates in the PE spectrum. In analogy to the above diene case, we find that the second EA band of COT^{+} is red-shifted (by 0.7 eV[9])) relative to 'parent' hexatriene cation (HT^{+}). It is

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[7]) B_γ describes the interaction between the terminal double bonds and was −0.06 eV in neutral COT. Since this interaction occurs mainly through intervening σ bonds in the nonplanar neutral molecule, it can safely be neglected for essentially planar COT^{+} where such interactions are probably very small.

[8]) This is to be expected in an LCBO ansatz, because π_2 actually has a zero coefficient for the central double bond and hence B_α is zero.

[9]) λ_{max} of HT^{+} in the presently used *Freon* mixture is at 392 nm (3.16 eV) [31].

tempting to apply the analogy which had worked so well for the dienes (similar shift of the HOMO→LUMO transition in the neutrals and the cations) to the present triene case. Surprisingly, λ_{max} of the two neutral compounds is very similar and, thus, one would expect no significant shift between the second bands of the two triene cations.

However, this inference is not valid, because the π systems of neutral HT and ionic $COT^{+\cdot}$ are planar while that of neutral COT is twisted around the 2–3 and 4–5 bonds ($\theta = 53°$, see above) which has the dual effect of lowering the HOMO and raising the LUMO (see *e.g.* the MNDO data in *Table 1*). Thus, one ought to base the prediction on the shift in λ_{max} between HT and *planar* COT which is of course not possible experimentally. MNDO predicts the HOMO/LUMO gap to decrease by 0.91 eV in going from HT to planar COT (actually to COT at the $COT^{+\cdot}$ equilibrium geometry) in good agreement with the observed 0.7 eV red shift between the second band of $HT^{+\cdot}$ and $COT^{+\cdot}$.

Conclusions. – The results presented above provide evidence on the following three points: *a)* Radical cations which are prone to facile rearrangements are efficiently prevented from undergoing such transformations, if ionization is effected in frozen *Freons* rather than in noble-gas matrices. This is illustrated by the example of BCO whose parent cation could not be identified in an Ar matrix due to extensive isomerization during ionization, whereas it is observed intact in a *Freon* glass. The reason for this phenomenon presumably lies in the synergetic operation of two effects: firstly, hole transfer from the (primarily ionized) solvent to the solute is less exothermic for *Freons* than for Ar due to their smaller ionization energies. Secondly, the excess energy imparted to the incipient solute cations is more readily quenched by polyatomic solvents which are better disposed to accept molecular vibrational quanta than noble-gas lattices.

b) The EA spectrum of $BCO^{+\cdot}$ is very similar to that of $CHD^{+\cdot}$ which shows that the π-electronic structure of the $CHD^{+\cdot}$ moiety suffers surprisingly little perturbation by the annellated four-membered ring. Taken together with the orbital diagram obtained by combining a butadiene with a cyclobutane fragment this shows that an earlier assignment of the UP spectrum of BCO had overlooked the π_1-MO which contributes to the second UP band.

c) Using π-bond basis energies and interaction parameters previously elaborated [13], the EA spectrum of $COT^{+\cdot}$ can only be interpreted satisfyingly, if it is assumed that the π system of COT undergoes planarization upon ionization. This contention is in accord with qualitative expectations, and it receives support from MNDO calculations on COT and $COT^{+\cdot}$. On the other hand, MINDO/3 is unable to account for this effect, as it predicts a planar structure for COT.

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Experimental Part

1,3,5-Cyclooctatriene (COT). 1,3,5,7-Cyclooctatetraene (*Fluka, purum*) was reduced under N_2 with Zn/EtOH/KOH with $PtCl_4$ as a catalyst according to *Jones* [22]. The resulting mixture of COT and BCO was separated by prep. GC (43 × 1 cm *Carbowax 20M* on *Chromosorb A-NA W 60–80,* 60° oven temp., t_R 12 min for BCO, 25 min for COT) which yielded 95% pure COT and ~ 91 % pure BCO (cap. GC and ^{2}H-NMR). While the COT was used directly, BCO was not obtained in sufficient quantity and purity for the envisaged experiments.

Bicyclo[4.2.0]octa-2,4-diene (BCO). The COT/BCO mixture was used to prepare BCO-$Fe(CO)_3$ applying a modification of the original procedure elaborated by *Manuel* and *Stone* [23]: 1.1 g (10.4 mmol) of COT/BCO and 2.92 g (15 mmol) of $Fe(CO)_3$ in 30 ml of degassed methylcyclohexane were heated under N_2 to 145° for 48 h. The resulting brown mixture was filtered over silica gel *60* to remove the Fe_2O_3 precipitate, whereupon the solvent and unreacted $Fe(CO)_3$ were removed *in vacuo.* The residual orange oil (2.34 g) was eluted with pentane from a 50 × 1-cm silica-gel *60* column. The first fraction contained 2.01 g (8.2 mmol, 79%) BCO-$Fe(CO)_3$ whose ^{2}H- and ^{13}C-NMR spectral were in accord with the expected structure. This material (1.86 g, 4.8 mmol) was dissolved in 6 ml of acetone, and 7.84 g (14.3 mmol) of $Ce(NH_4)(NO_3)_6$ in 19 ml of acetone were added dropwise at −15°, whereby CO_2 was evolved. After standing at r.t. for 1.5 h, 15 ml of pentane were added, and the resulting mixture was extracted 4 times with 25 ml of sat. aq. NaCl and 8 times with 5 ml of deionized H_2O in order to remove inorg. material and acetone. After drying the pentane soln., a GC analysis (2 m × 4 mm ODPN 25% on *Chromosorb W,* 60°) showed next to 0.3% of acetone a 97:3 mixture of BCO and COT. Since it proved impossible to separate BCO from pentane by distillation, prep. GC was used to obtain pure samples. BCO was now the main component.

Method and Instruments. Solns. (5×10^{-3} M) of the hydrocarbons in a 1:1 mixture of $CFCl_3$ and CF_2Br-CF_2Br [24], which was dried by distillation over CaH_2 and storage over molecular sieve, were filled into home-built Cu cuvettes fitted with quartz windows [31] and cooled to 77 K to form a transparent glass. After ~ 0.5 Mrad γ-irradiation in a ^{61}Co *Gammacell 220* source, the cuvettes, were introduced into a spectral quartz dewar equipped with a Cu sample holder [31], and UV/VIS/NIR spectra were recorded on a *PE Lambda 9* spectrometer interfaced to a *PE 3600* data station. UP spectra were recorded on a modified *PE 16* instrument operated in preretardation mode [32] and calibrated with MeI.

Calculations. Semiempirical calculations were done with the MOPAC program package [33], while the *ab initio* wave functions were obtained from *Gaussian 82* [34]. MO's were drawn using a version of the MOPLOT program [35] adapted to run on *Olivetti M24* PC's [36].

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