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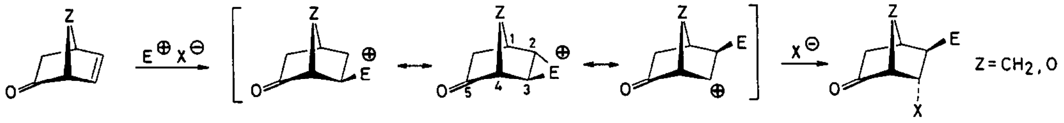
THE CARBONYL GROUP AS HOMOCONJUGATED ELECTRON DONATING SUBSTITUENT.
AB INITIO STO 3G MO CALCULATIONS.

Pierre-Alain Carrupt and Pierre Vogel*

Institut de chimie organique de l'Université, 2, rue de la Barre,
CH-1005 Lausanne, Switzerland.

Summary. *ab initio STO 3G calculations on 2,3-episulfonionorbornanes and 2-norbornyl cations substituted at C(5) or C(6) suggest that homoconjugated carbonyl group and related (-M, -I) functions can be remote electron-donors.*

Under kinetic control, 2-bicyclo[2.2.1]hept-5-enone (2-norborn-5-enone)[1], 7-oxa-2-norborn-5-enone[2] and 2-bicyclo[2.2.2]oct-5-enone[1] add soft electrophiles with high regioselectivity as shown for 1 + EX → 5. The nucleophile, X^-, prefers to attack carbon centre C(3) of intermediate 3 because the limiting structure 4 is favoured over structure 2. The carbonyl group stabilizes 4 because of its polarizability which can be interpreted in terms of homoconjugation 6 ↔ 7 and/or hyperconjugation 7 ↔ 8 (n(CO)↔ σC(4),C(5) ↔ pC(2), see 9).[3] These electron donating interactions overwhelm the destabilizing field effect of the oxo group. These hypotheses, as well as a large body of experimental results,[1,3] seem in excellent accord with the recent report of Snow and Williams[8] on radical-cations of carbonyl compounds which show "enhanced" proton hyperfine couplings for γ-C-H bonds aligned with the carbonyl group, as shown in 10.



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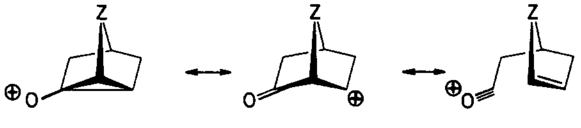

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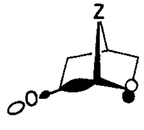

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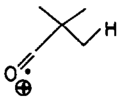

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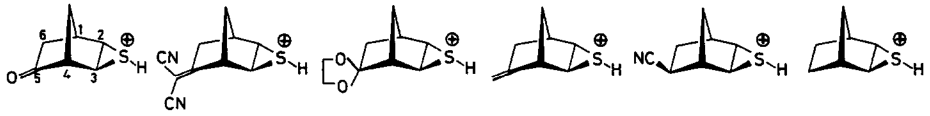
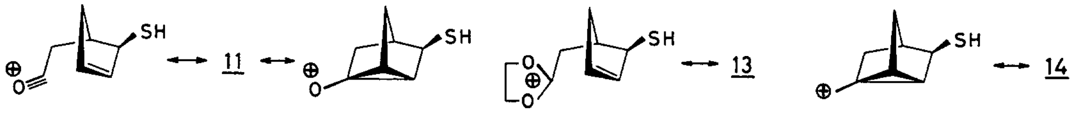
The C(3)-E^+ bond in 3 should be slightly longer than the C(2)-E^+ bond. This hypothesis is now confirmed by the completely minimized geometry of 5-oxo-2,3-exo-episulfonionorbornane cation (11), as obtained by the ab initio STO 3G MO method. We also report calculations on cations 12-16 (Table 1) and on substituted 2-norbornyl cations 21-31 (Table 2) which suggest that homoconjugated methylene and ethylenedioxy groups can also act as electron donors. The dicyanomethylene substituent can be either electron donating or electron withdrawing when homoconjugated with a carbocation, depending on electron demand.

Table 1. Ab initio STO 3G minimized geometries of episulfonium cations 11-16. Bond lengths in Å.[9,10]



bond	11	12	13	14	15	16
C(1)-C(2)	1.546	1.546	1.544	1.544	1.544	1.543
C(2)-S^+	1.869	1.868	1.870	1.870	1.870	1.871
C(3)-S^+	1.873	1.867	1.875	1.877	1.867	1.871
C(3)-C(4)	1.541	1.549	1.539	1.547	1.543	1.543
C(4)-C(5)	1.573	1.540	1.510	1.542	1.572	1.561
C(6)-C(1)	1.556	1.561	1.556	1.561	1.560	1.561
C(6)-C(2)	2.438	2.438	2.429	2.434	2.434	2.431
C(5)-C(3)	2.409	2.390	2.441	2.393	2.435	2.430
E_{tot}(hartrees)	-733.9147	-879.7145	-884.9751	-698.6324	-751.8053	-661.2732

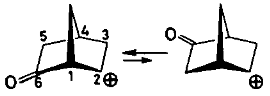
The difference in bond length between C(3)-S^+ and C(2)-S^+ in 11 is calculated to be 0.004 Å. Although very small, it is indicative of the contribution from limiting structures 11 ↔ 17 to the stabilization of the ion. This interpretation is confirmed by the "extra" long C(4)-C(5) bond (1.573 Å) in 11, which should be compared with that calculated for 12 (1.54 Å). The data suggest that homoconjugation 11 ↔ 18 is of little importance. This is further confirmed by the calculated geometry of ethyleneacetal 13, which exhibits the same features as found for 11. The hyperconjugation 13 ↔ 19 renders the ethylenedioxy substituent in 13 electron donating, just as with the carbonyl group in 11. This is in agreement with our experimental results on the electrophilic additions to 5,5-ethylenedioxy-2-norbornene.[1] The C(4)-C(5) bond elongation calculated in 11 and 13 is also consistent with the formation of products from C(4)-C(5) bond breakage upon electrophilic addition to 2-norborn-5-enone and its acetals.[1,11]

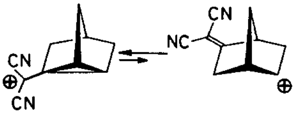


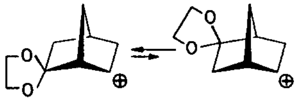
17 18 19 20

As expected,[12] the 5-methylene group in episulfonium ion 14 acts as an electron donating substituent due to homoconjugation 14 ↔ 20. In agreement with this hypothesis the C(3)-S^+ bond in 14 is 0.007 Å longer than the C(2)-S^+ bond. Furthermore, the C(3)-C(5) distance is significantly reduced in comparison with that in 15 and 16. For 12, the C(3)-S^+ and C(2)-S^+ bonds are calculated to have practically the same length, in agreement with the absence of regioselectivity in the additions of arenesulfenyl and areneselenyl halides to 5-dicyanomethylene-2-norbornene.[13] As expected,[1] the 5-exo-cyano substituent in 15 acts as an electron withdrawing group, thus making the C(2)-S^+ bond slightly longer than the C(3)-S^+ bond. The capability of the carbonyl, ethylenedioxy and methylene groups, in 11, 13 and 14, respectively, to act as homoconjugated electron donors has been further tested by ab initio STO 3G calculations on substituted 2-norbornyl cations 21-31 (Table 2)[14] which are models for limiting structures 2 and 4.

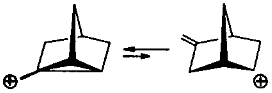
Table 2. Ab initio STO 3G minimized geometries of cations 21-31. Bond lengths in Å.[9] Calculated relative hydride affinities in kcal/mol; $\Delta HA = E_{tot}(R^+) - E_{tot}(RH) - E_{tot}$(2-norbornyl cation) + E_{tot}(norbornane).

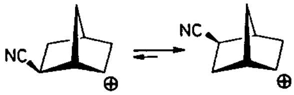






bond	21	22	23	24	25	26
C(1)-C(2)	1.427	1.486	1.443	1.488	1.435	1.479
C(1)-C(6)	1.715	1.593	1.669	1.596	1.731	1.599
C(2)-C(6)	2.247	2.338	1.669	2.347	2.403	2.306
C(4)-C(5)	1.546	1.554	1.550	1.530	1.546	1.576
ΔHA	2.7	9.7	10.7	18.6	-3.5	0.8





	27	28	29	30	31
C(1)-C(2)	1.440	1.479	1.488	1.479	1.473
C(1)-C(6)	1.665	1.605	1.611	1.555	1.610
C(2)-C(6)	1.665	2.316	2.358	2.307	2.285
C(4)-C(5)	1.548	1.531	1.550	1.561	1.550
ΔHA	-16.5	1.6	13.4	11.2	0

As suggested by our experimental results[1] and our calculations on episulfonium ions 11, 13 and 14, the homoconjugated carbonyl, ethylenedioxy and methylene groups act as electron donors, thus rendering the 6-substituted 2-norbornyl cations 21, 25 and 27, respectively, more stable than the corresponding 5-substituted isomers 22, 26 and 28. In 21 and 25, relatively long C(1)-C(6) and short C(1)-C(2) bonds are calculated in agreement with a hyperconjugative stabilizing interaction of the $n(O) \leftrightarrow \sigma C(1,6) \leftrightarrow pC(2)$ type (e.g. 7 ↔ 8, 13 ↔ 19). As expected,[12] 6-methylene-2-norbornyl cation has the symmetrical (C_s) structure of nortricyclylmethyl cation 27. Strikingly, this is also the case with the 5-dicyanomethylene-2-norbornyl cation 23. The stability difference between 27 and 28 is calculated to be near 18 kcal/mol. With 23 and 24 it is lowered to ca. 8 kcal/mol due to the field effect of the carbonitrile groups. This destabilizing effect is, however, not sufficent to render the 5-dicyanomethylene-2-norbornyl cation (24) more stable than its isomer 23. The electron-donating ability of the carbonitrile group α to a carbenium ion has been well documented.[17] Because of strong electron demand in the "isolated" 2-norbornyl cation derivative 23, the homoconjugated dicyanomethylene group acts as electron donor. In the more delocalized episulfonium ion 12, the electron-withdrawing effect (field effect) is competitive. In accord with its inductive effect, the cyano group destabilizes the 2-norbornyl cation more when in the exo-6 rather than in the exo-5 position.[18]

The calculation reported here confirm the hypothesis that a remote substituent, which would normally destabilize a positively charged species because of its inductive (field) effect, can also act as electron donor if the electron demand is large enough.[19] In the case of homoconjugated substituents, the stabilizing effect can be associated with a through space, (homoconjugative) interaction and/or with a through-bond (hyperconjugative) interaction. For homoconjugated carbonyl and ethylenedioxy group the $n(O),\sigma \leftrightarrow \pi$ interaction may dominate.[20]

Acknowledgment. We are grateful to Hoffmann-La Roche and Co., Basel, to the "Swiss National Science Foundation" and to the "Ecole Polytechnique Fédérale de Lausanne", for generous support.

Footnotes and references.

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