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Homoconjugation Interactions between Occupied and Unoccupied Molecular Orbitals. II

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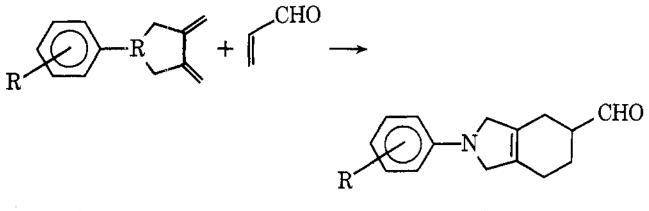
Perturbation molecular orbital theory is used to explain the homoconjugation interactions in systems in which the respective frontier molecular orbitals of the π moieties are of opposite symmetry. The theory predicts a hypsochromic shift in the uv wavelength maximum for such systems from reference compounds. No cases of unambiguous bathochromic λ_{max} shifts were found in the literature to contrast with the theory's prediction. Inductive effects and hyperconjugation were not the origin of the hypsochromic shifts. The prediction of uv data and photoelectron spectroscopy concerning through-space interactions is compared.

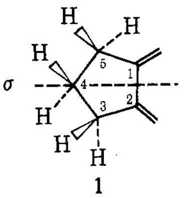
Homoconjugation between nonconjugated π-electron systems has received considerable attention over the last decade.[1] More recently, through-bond and hyperconjugation interactions have been shown to have an important role in certain cases.[1c–e,2] The use of perturbation molecular orbital theory to explain the homoconjugation in systems in which the respective frontier molecular orbitals (MO's) of the π moieties are of the same symmetry was demonstrated by Hofmann et al.[1d,e] Recently, we used the perturbation molecular orbital approach to explain the novel substituent effect in the Diels–Alder reaction between 1-(substituted phenyl)-3,4-dimethylenepyrrolidine, homoconjugated diene, and acrolein.[3] The respective frontier MO's of the π moieties of this exocyclic diene are of opposite symmetry (symmetric or asymmetric) with respect to the plane of symmetry which bisects the molecule. In this paper a general theory for predicting the effect of homoconjugation on the energy separation of the frontier MO's of π moieties whose respective frontier MO's are of opposite symmetry is developed.



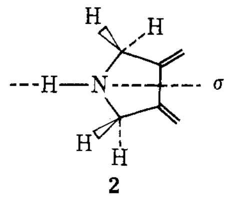
Theory

The fundamentals of perturbation molecular orbital theory are as follows. (1) When two molecular orbitals interact (the molecular orbitals must be of the same symmetry), the lower energy molecular orbital is stabilized and the higher energy molecular orbital is destabilized. (2) The smaller the energy separation between the interacting molecular orbitals, the greater the interaction.

The application of this theory to homoconjugation systems with π moieties, whose respective frontier MO's are of opposite symmetry with respect to the plane of symmetry which bisects the molecule, will be first illustrated by the exocyclic dienes 1,2-dimethylenecyclopentane (1) and 3,4-dimethylenepyrrolidine (2). The relative energies of the frontier MO's of 1 and 2 are determined from orbital interaction diagrams of the CNDO/2 frontier MO's of 2,3-dimethyl-1,3-butadiene with those of methane[4] and ammonia. In 1, both frontier MO's of methane (4-methylene moiety) interact with the LUMO of the hyperconjugated butadiene (Figure 1). The interaction between the σ^* and the LUMO-butadiene is more important; thus, a small decrease in the LUMO energy of 1 is expected as compared to *cis*-2,3-dimethyl-1,3-butadiene. However, the substitution of a heteroatom as in 2 for the 4-methylene moiety of 1 will replace the above molecular orbital interactions with a single molecular orbital interaction between the nonbonded



1



2

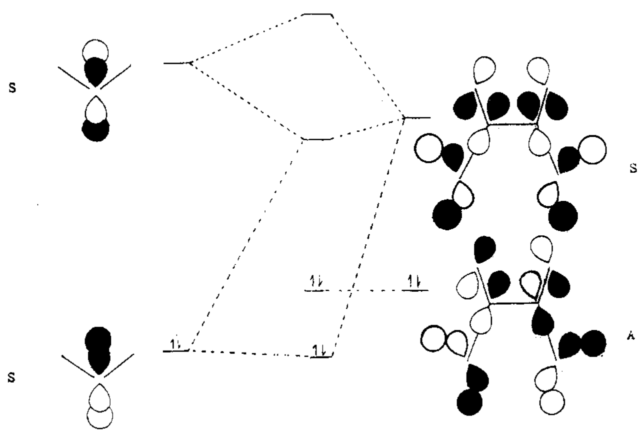


Figure 1. Relative energies of the frontier MO's of 1,2-dimethylenecyclopentane from the interaction of the CNDO/2 frontier MO's of methane and 2,3-dimethyl-1,3-butadiene.

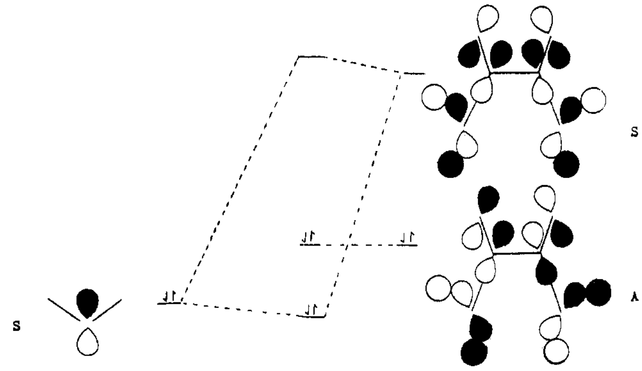
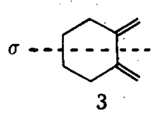


Figure 2. Relative energies of the frontier MO's of 3,4-dimethylenepyrrolidine from the interaction of the CNDO/2 frontier MO's of ammonia and 2,3-dimethyl-1,3-butadiene.

orbital[5] of the heteroatom and the LUMO of the hyperconjugated butadiene (Figure 2). This MO interaction will raise the LUMO of **2** in energy as compared to *cis*-2,3-dimethyl-1,3-butadiene. Consequently, **2** is predicted to have a greater energy separation between its frontier MO's than is **1**.

To provide additional assurance that the above postulated effect is present, the relative energies of the frontier MO's of these exocyclic dienes were also determined from orbital interaction diagrams of the CNDO/2 frontier MO's of butadiene with those of propane and dimethylamine. The MO interactions between the frontier MO's of these compounds were also such as to produce a greater energy separation between the frontier MO's of **2**. The HOMO of both dimethylamine and propane interacted only with the LUMO of butadiene. This interaction was greater with dimethylamine because its HOMO (−0.498 au) was of considerably higher energy than the HOMO (−0.570 au) of propane. Also, the calculations predict that dimethylamine has one less unoccupied MO than does propane and the absent unoccupied MO corresponds to the LUMO (0.275 au) of propane which by symmetry interacts with the LUMO of butadiene.

Another situation which is encountered frequently is the replacement of an ethane moiety with an ethylene moiety as in 1,2-dimethylenecyclohexane (**3**) and 1,2-dimethylene-4-cyclohexene (**4**). The respective CNDO/2 frontier MO's of ethane[6] and ethylene are of opposite symmetry with respect to a symmetry plane that is perpendicular to and bisects the carbon–carbon bond of the molecule. The HOMO-ethane moiety interacts with the HOMO-hyperconjugated butadiene and the LUMO-ethane moiety interacts with the LUMO-hyperconjugated butadiene in **3**; consequently, the energy separation between the frontier MO's of **3** is expected to be less than that of *cis*-2,3-dimethyl-1,3-butadiene (Figure 3). In **4**, the HOMO-ethylene moiety interacts with the LUMO-hyperconjugated butadiene and the LUMO-ethylene moiety interacts with the HOMO-hyperconjugated butadiene; consequently, the frontier MO energy separation of **4** is expected to be greater than that of *cis*-2,3-dimethyl-1,3-butadiene (Figure 4). Thus, the replacement of an ethane moiety with an ethylene moiety as in **3** and **4** is predicted to increase the energy separation between the frontier MO's of the diene moiety.



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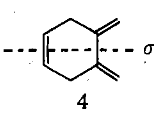

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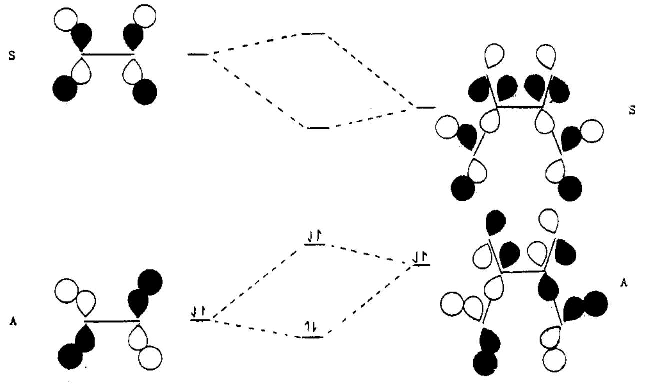


Figure 3. Relative energies of the frontier MO's of 1,2-dimethylenecyclohexane from the interaction of the CNDO/2 frontier MO's of ethane and 2,3-dimethyl-1,3-butadiene.

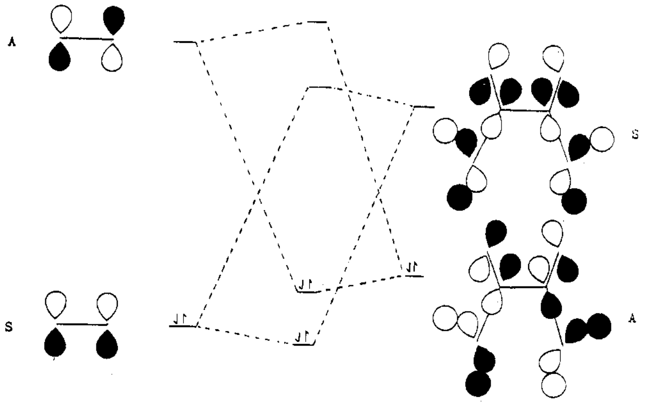


Figure 4. Relative energies of frontier MO's of 1,2-dimethylene-4-cyclohexene from the interaction of the CNDO/2 frontier MO's of ethylene and 2,3-dimethyl-1,3-butadiene.

CNDO/2 calculations[7] on various model systems predict the above discussed MO interactions. The CNDO/2 calculations were carried out on ethane, ethylene, 1,2-dimethylenecyclohexane, 1,2-dimethylene-4-cyclohexene, methane, water, ammonia, hydrogen sulfide, 2,3-dimethyl-1,3-butadiene, 1,2-dimethylenecyclopentane, 3,4-dimethylenetetrahydrofuran, 3,4-dimethylenepyrrolidine, and 3,4-dimethylenethiophane.

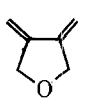
The energy of uv transitions are calculated in SCF methods from eq 1.[8]

$$\Delta E = \epsilon_j - \epsilon_i - J_{ij} + 2K_{ij} \qquad (1)$$

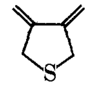
In this expression, ϵ_j and ϵ_i are the energies of an occupied MO and an unoccupied MO, respectively, while J_{ij} and K_{ij} are the coulomb and exchange integrals which account for the difference in electron repulsion in the ground and excited states. Consequently, homoconjugation of the type discussed can be verified experimentally by hypsochromic λ_{max} shifts from reference compounds if the two-electron effects are smaller or reinforce the one-electron effects.

Results and Discussion

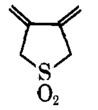
Experimental data in Table I indicate the possibility of a small hypsochromic λ_{max} shift in **5** and **6** from the reference compounds **1** and **7**, while 3,4-dimethylenethiophane (**8**) exhibits a larger λ_{max} shift. Furthermore, when the nonbonded electrons of the sulfur of **8** become bonded in a sulfone group (**9**) and a sulfoxide group (**10**), the expected bathochromic shift is observed.



5
λ_{max} 244 nm



8
λ_{max} 240 nm



9
λ_{max} 244 nm

Homoconjugation is also observed in the thiophene system (Table I). A hypsochromic shift of 12 nm is observed for 1*H*,3*H*-thieno[3,4-*c*]thiophene (**11**) from the reference compound, cyclopenta[c]thiophene (**12**). When the sulfur heteroatom is oxidized to the sulfone (**13**), the expected bathochromic shift is again observed. However, homoconjugation is not observed with the nitrogen and oxygen heteroatoms, **14** and **15**.

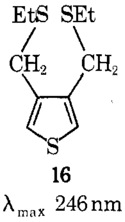
11
λ_{max} 232 nm

12
λ_{max} 244 nm

13
λ_{max} 244 nm

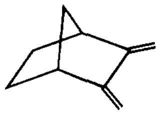
The larger λ_{max} shift observed in the diene and the thiophene moieties that are homoconjugated with sulfur rather than with nitrogen and oxygen is probably due to the greater overlap between the nonbonded π orbital of sulfur and the carbon 2p orbitals of the thiophene and the diene moieties. In support of this hypothesis, Schmidt and Schweig observed by photoelectron spectroscopy a large through-space interaction between the π moieties of 2,5-dihydrothiophene, but none in 2,5-dihydrofuran.[9] Also, the CNDO/2 resonance and overlap integrals at 2.5 and 3.0 Å support this hypothesis (Table II).[10] Experimental ionization potentials of model compounds of the heteroatom moieties rule out the orbital energies as the origin of the larger shifts.[11,12] Also, CNDO/2 calculations predict an interaction between the d orbitals of the sulfur moiety and the frontier MO's of the thiophene and the diene moieties. This additional interaction could also contribute to the larger λ_{max} shifts.

Hyperconjugation and inductive effects could be the origin of the hypsochromic shifts observed in the exocyclic diene and thiophene systems. If they were, an even larger hypsochromic λ_{max} shift would be expected in 3,4-bis(ethylthio)methylthiophene (**16**) from the reference compound **12**. However, a bathochromic shift is observed. Furthermore, the oxidation of the homoconjugation sulfur to a sulfone gave a bathochromic shift in both systems as would be expected if through-space orbital interactions are the origin of the λ_{max} shifts. Also, the replacement of the methylene group with a heteroatom should give the hypsochromic λ_{max} shifts in every case if hyperconjugation and inductive effects are its origin. This is expected because the overlap between the orbitals of the heteroatoms and the adjacent methylene groups is significant in all cases. The CNDO/2 resonance and overlap integrals at 1.5 Å support this hypothesis (Table II).[10]

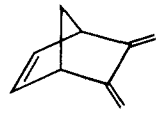


16
λ_{max} 246 nm

The predicted hypsochromic λ_{max} shift was not observed in the cyclohexane system (**3**, **4**, **17**) because of the nonplanarity of the diene moiety[13] of 1,2-dimethylenecyclohexane whose effect dominates the possible homoconjugation. However, homoconjugation is observed in the analogous bicyclo[2.2.1]heptane system (**18–23**) in which the diene moiety is rigidly held in the cisoid planar conformation.

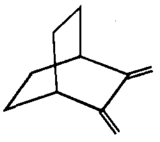


18
λ_{max} 248 nm

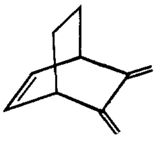


19
λ_{max} 240 nm

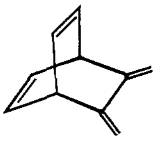
In the bicyclo[2.2.2]octane and tricyclo[4.2.2.0^{2,5}]decane systems, the hypsochromic shift is small or not present when the diene moiety is homoconjugated with one double bond moiety (**24–28**). However, a 10-nm hypsochromic shift is observed by Butler and Snow[14] when the diene moiety is homoconjugated with two double bond moieties (**29**).



25
λ_{max} 252 nm

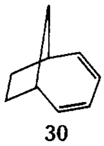


24
λ_{max} 252 nm

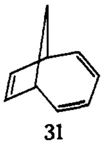


29
λ_{max} 242 nm

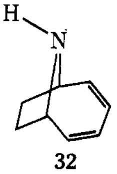
The predicted hypsochromic λ_{max} shift is observed in the bicyclo[4.2.1]nona-2,4-diene and 2,4,7-triene systems. The homoconjugated compounds **32–34** have shorter wavelength maxima than the reference compound, bicyclo[4.2.1]nona-2,4-diene (**30**). Furthermore, the smaller shift observed when electron-withdrawing groups are attached to the nitrogen heteroatom is expected since these groups lower the energy of the nonbonded orbital of the heteroatom thereby decreasing its interaction with the LUMO of the diene moiety. The homoconjugated compounds **35–38** also have shorter wavelength maxima than the reference compound, bicyclo[4.2.1]nona-2,4,7-triene (**31**). The predicted homoconjugation interaction in the bicyclo[4.2.1]diene system is in contrast to photoelectron data which has been interpreted as indicating no homoconjugation between the π moieties.[15] Furthermore, comparison of the wavelength maxima in compounds **30** and **31** indicates no significant homoconjugation interactions between the π



30
λ_{max} 259 nm



31
λ_{max} 257 nm



32
λ_{max} 248 nm

Table I. Ultraviolet Spectral Data of Homoconjugated and Reference Compounds

No.	Compd	λ_{max}, nm (ϵ)	Solvent	Ref
1	1,2-Dimethylenecyclopentane	243	C_6H_{12}	*a*
		248 (10 500)	Isooctane	*b*
3	1,2-Dimethylenecyclohexane	218 (7602)	No solvent given	*c*
		220 (6375)	95% EtOH	*d*
4	1,2-Dimethylene-4-cyclohexene	216	No solvent given	*e*
		219 (5340)	95% EtOH	*d*
5	3,4-Dimethylenetetrahydrofuran	244 (9820)	Isooctane	*a*
6	1-Methyl-3,4-dimethylenepyrrolidine	245 (8700)	Isooctane	*f*
7	1,2-Dimethylene-3-methylcyclopentane	248 (8510)	Isooctane	*b*
8	3,4-Dimethylenethiophane	240 (6000)	95% EtOH	*g*
9	3,4-Dimethylenethiophane 1,1-dioxide	244 (6680)	95% EtOH	*g*
10	3,4-Dimethylenethiophane 1-oxide	244 (6150)	95% EtOH	*g*
11	1*H*,3*H*-Thieno[3,4-*c*]thiophene	232 (6100)	95% EtOH	*h*
12	Cyclopenta[*c*]thiophene	244 (7370)	95% EtOH	*i*
13	1*H*,3*H*-Thieno[3,4-*c*]thiophene 2,2-dioxide	244 (6400)	95% EtOH	*j*
14	4*H*,6*H*-5-Ethylthieno[3,4-*c*]pyrrole	242.5 (6200); 232.5 (5900)	95% EtOH	*j*
15	1*H*,3*H*-Thieno[3,4-*c*]furan	244 (6600)	95% EtOH	*k*
16	3,4-Bis[(ethylthio)methyl]thiophene	246 (5600)	95% EtOH	*h*
17	1,2-Dimethylene-4-methyl-4-cyclohexene	218 (5340)	95% EtOH	*d*
18	2,3-Dimethylenebicyclo[2.2.1]heptane	248 (10 600)	C_6H_{12}	*a*
		249 (11 510)	No solvent given	*c*
		248 (8900)	EtOH	*l*
19	2,3-Dimethylenebicyclo[2.2.1]hept-5-ene	241 (9560)	95% EtOH	*d, m*
		240 (8900)	EtOH	*l*
20	7-Isopropylidene-2,3-dimethylenebicyclo-[2.2.1]hept-5-ene	246 (12 900)	EtOH	*l*
21	7-Isopropylidene-2,3-dimethylenebicyclo-[2.2.1]heptane	250 (1200)	EtOH	*l*
22	2,3-Dimethylenebicyclo[2.2.1]hept-5-ene-7-spiro-1′-cyclopropane	241.5 (9550)	EtOH	*l*
23	2,3-Dimethylenebicyclo[2.2.1]heptane-7-spiro-1′-cyclopropane	247.5 (9300)	EtOH	*l*
24	2,3-Dimethylenebicyclo[2.2.2]octane	247 (10 000)	95% EtOH	*d*
		249 (8390)	No solvent given	*c*
		247 (7600); 252 (7600)	EtOH	*l*
25	2,3-Dimethylenebicyclo[2.2.2]oct-5-ene	253 (6650)	No solvent given	*m*
		246 (8100); 252 (8100)	EtOH	*l*
26	2,3-Dimethylene-5-methyl-8-isopropyl-bicyclo[2.2.2]oct-5-ene	246 (8350)	95% EtOH	*d*
27	9,10-Dimethylenetricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene	247 (7900)	EtOH	*l*
28	9,10-Dimethylenetricyclo[4.2.2.$0^{2,5}$]dec-3-ene	249.5 8300)	EtOH	*l*
29	2,3-Dimethylenebicyclo[2.2.2]octa-5,7-diene	242 (9100)	C_6H_{12}	*l*
30	Bicyclo[4.2.1]nona-2,4-diene	259	EtOH	*n*
31	Bicyclo[4.2.1]nona-2,4,7-triene	259 (2691); 268 (2455); 278 sh (1349)	C_6H_{12}	*o*
		257	No solvent given	*p*
32	9-Azabicyclo[4.2.1]nona-2,4-diene	248 (2200)	CH_3CN	*q*
33	*N*-Cyano-9-azabicyclo[4.2.1]nona-2,4-diene	257 (4630)	CH_3CN	*q*
34	*N*-Carbamoyl-9-azabicyclo[4.2.1] nona-2,4-diene	255 (1500)	CH_3CN	*q*
35	9-Azabicyclo[4.2.1]nona-2,4,7-triene	245 (2300)	C_6H_{12}	*q*
36	*N*-Cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene	255	CH_3CN	*r*
37	*N*-Carbamoyl-9-azabicyclo[4.2.1]nona-2,4,7-triene	255 (1980)	CH_3OH	*q*
38	*N*-Carboethoxy-9-azabicyclo[4.2.1]nona-2,4,7-triene	252 (2200)	C_6H_{12}	*q*
39	Bicyclo[4.2.1]nona-2,4,7-trien-9-one	267 (3000); 276 (2800); 320 (630)	CH_3OH	*s*
40	Bicyclo[4.2.1]nona-2,4-dien-9-one	264 (3300); 313 (500)	CH_3OH	*s*

Footnotes to Table I

[a] W. J. Bailey and S. S. Miller, *J. Org. Chem.*, **28,** 802 (1963), and references cited therein. [b] A. T. Blomquist, J. Wolinsky, Y. C. Meinwald, and D. T. Longone, *J. Am. Chem. Soc.*, **78,** 6057 (1956). [c] K. Alder and H. Molls, *Chem. Ber.*, **89,** 1960 (1956). [d] J. M. Garrett, Ph.D. Thesis, University of Texas, Austin, Texas, 1966. [e] C. S. Manuel and E. E. Ryder, *J. Am. Chem. Soc.*, **77,** 66 (1955). [f] Y. Gaoni, *Tetrahedron Lett.*, 2361 (1973). [g] S. Sadeh and Y. Gaoni, *ibid.*, 2365 (1973). [h] H. Wynberg and D. J. Zwanenbury, *J. Org. Chem.*, **29,** 1919 (1964). [i] D. W. H. MacDowell, T. B. Patrick, B. K. Frame, and D. L. Ellison, *J. Org. Chem.*, **32,** 1226 (1967). [j] D. J. Zwanenburg and H. Wynberg, *J. Org. Chem.*, **34,** 333 (1969). [k] D. J. Zwanenburg and H. Wynberg, *J. Org. Chem.*, **34,** 340 (1969). [l] Reference 13. [m] K. Alder, S. Hartung, and O. Netz, *Chem. Ber.*, **90,** 1 (1957). [n] C. W. Jefford and F. Delay, *Helv. Chim. Acta*, **56,** 1083 (1973). [o] H. Tsuruta, K. Kurabayashi, and T. Mukai, *Tetrahedron Lett.*, 3775 (1967). [p] L. G. Cannell, *Tetrahedron Lett.*, 5967 (1966). [q] A. G. Anastassiou and R. P. Cellura, *J. Org. Chem.*, **37,** 3126 (1972). [r] A. G. Anastassiou, *J. Am. Chem. Soc.*, **90,** 1527 (1968). [s] D. I. Schuster and C. W. Kim, *J. Org. Chem.*, **40,** 505 (1975).

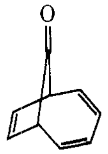
Table II. CNDO/2 Resonance (β) and Overlap (S) Integrals[a]

	pπ, pπ overlap						pσ, pσ overlap					
r, Å	S_{CN}	S_{CO}	S_{CS}	$-\beta_{CN}$	$-\beta_{CO}$	$-\beta_{CS}$	S_{CN}	S_{CO}	S_{CS}	$-\beta_{CN}$	$-\beta_{CO}$	$-\beta_{CS}$
1.5	0.1573	0.1197	0.2579	3.618	3.112	5.048	0.3094	0.2711	0.3455	7.116	7.049	6.763
2.5	0.0173	0.0108	0.0416	0.398	0.281	0.814	0.0859	0.0589	0.1705	1.976	1.531	3.338
3.0	0.0051	0.0029	0.0144	0.117	0.075	0.282	0.0331	0.0205	0.0804	0.761	0.533	1.574

[a] Resonance integral is in eV.

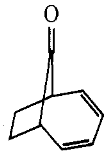
moieties of **31**. In this case, the uv data and photoelectron data are consistent.[16]

To further demonstrate the usefulness of the uv wavelength maximum method, this approach will be applied to compounds **39** and **40** in which a bathochromic λ_{max} shift is observed when compared respectively to reference compounds, **31** and **30**. This shift must originate from the orbital interaction of the asymmetric nonbonding π orbital of the oxygen and the asymmetric HOMO of the diene because the other through-space interactions, LUMO-diene with HOMO-carbonyl and LUMO-diene with LUMO-carbonyl, have opposite effects on the HOMO–LUMO diene energy separation.[17] Further, the nonbonded π orbital must be of lower energy than the HOMO of the diene since the shift is bathochromic. Analysis of **39** by photoelectron spectroscopy confirms this rationale.[18]



39

λ_{max} 267 nm



40

λ_{max} 264 nm

Conclusion

The theoretical approach presented in this paper accounts for the hypsochromic λ_{max} shifts observed in many homoconjugation systems. In no case was an unambiguous bathochromic λ_{max} shift found in the literature to contrast with the theory's prediction. Inductive effects and changes in hyperconjugation do not appear to significantly alter the frontier orbital separation of the moieties.[19] Also, the detection of through-space interactions appeared to be just as reliable with the uv method as with photoelectron spectroscopy and the uv method has an advantage in that changes in the energy level of unoccupied MO's can be detected. Finally, since the stabilization obtained from the homoconjugation is small (<2 kcal/mol), steric effects will reduce this interaction in some cases.

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Registry No.—1,2-Dimethylenecyclopentane, 20968-70-1; methane, 74-82-8; 2,3-dimethyl-1,3-butadiene, 513-81-5; 3,4-dimethylenepyrrolidine, 50586-16-8; ammonia, 7664-41-7; 1,2-dimethylenecyclohexane, 2819-48-9; ethane, 74-84-0; 1,2-dimethylene-4-cyclohexene, 54290-41-4; ethylene, 74-85-1.

References and Notes

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(4) Only the hyperconjugation frontier MO's of methane are used in the orbital interaction diagram because of their greater overlap with the butadiene π MO's.

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(10) The sulfur moiety is probably ~0.35 Å further from the thiophene and the diene moieties than the nitrogen and oxygen moieties because of the longer carbon–sulfur bond length.

(11) The ionizational potentials[12] of the model compounds are as follows: methane, 12.6 eV; ammonia, 10.2 eV; water, 12.6 eV; hydrogen sulfide, 10.4 eV.

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(17) Symmetry of the MO's were determined from the mirror plane which bisects the molecule.

(18) H. Schafer, H. Schmidt, A. Schweig, R. W. Hoffmann, and H. Kurz, *Tetrahedron Lett.*, 1953 (1975).

(19) After submission of this manuscript, a paper by Gergely, Akhavin, and Vogel [*Helv. Chim. Acta.*, **58,** 871 (1975)] was published which explained the hypsochromic uv shift in a limited series of similar compounds mainly in terms of hyperconjugation of the diene moiety with the σ skeleton of the bicyclic system. The compounds given in this paper are in agreement with our theory. The hypsochromic shift observed in 2,3-dimethylene-5,6-*exo*-epoxynorbornane and 2,3-dimethylene-5,6-*exo*-epoxy-7-oxanorbornane is predicted from the interactions of the CNDO/2 MO's of the ethylene oxide and ethane moieties with the MO's of **1** and **5**. Furthermore, the approach of Gergely et al. does not account for the absence of the hypsochromic shift in compounds **14, 15, 16, 25,** and **31** nor for the bathochromic shift in **9, 10,** and **13**.