Table I. ^{14}N hf Couplings for the NO_2 Groups in DPPH

technique	A^N_{ortho}, G	A^N_{para}, G	ref
computer simulation of EPR spectra	0.754	0.377	13
Fourier transform analysis of EPR	0.38	0.33	14
combined EPR and proton ENDOR	1 ± 0.3	0.7 ± 0.3	4
theoretical values using Hartree-Fock spin densities plus			
(a) Karplus-Fraenkel approach	−1.56	−1.14	4, 5, 10, 11
(b) Nanda et al. approach	−0.27	−0.25	4, 5, 10, 12
CW NMR at 4.3 MHz and computer simulation	−0.46 ± 0.02	−0.38 ± 0.02	8
	−0.39 ± 0.02	−0.48 ± 0.02	8
FT NMR at 13.0 MHz	−0.38 ± 0.02	−0.48 ± 0.03	this work

other peak. If, however, the higher intensity NMR signal corresponds to the two ortho nitrogens, then an increase in temperature above 250 K would lead to either further narrowing or no change in the spectra. Figure 1a–d shows the latter to be the case, thereby establishing that $A^N_{ortho} = -0.38 \pm 0.02$ G and $A^N_{para} = -0.48 \pm 0.03$ G.

However, the assignment of $A^N_{para} > A^N_{ortho}$ is in conflict with the current theoretical models for estimating ^{14}N hf couplings,[10–12] since all these calculations predict[8] that $A^N_{para} < A^N_{ortho}$. The reliability of the reported spin densities was suggested by a very good agreement between the calculated[10–12] and the observed values[4,5] for the proton hf couplings in DPPH. The disagreement for the ^{14}N results suggests that the ^{14}N couplings can provide a very sensitive probe of the accuracy of the wave functions for large free radicals. Table I shows a comparison of the results from various techniques.

The temperature dependence of the observed line widths of the o-NO_2 signal was studied over 230–343 K. The line width decreased sharply with the increase in temperature, indicating motional narrowing. The line-width variation could be analyzed by employing the modified Bloch equations.[15] In the regime of "fast" motion, the line broadening, $\delta\omega$, caused by motional effects is given by[15]

$$\ln(\delta\omega) = \ln[(\Delta W)^2/(8P_0)] + E_a/(kT)$$

E_a being the activation energy and the other symbols having usual meanings. Thus if motional effects are the dominant cause of line broadening, then the plot of $\ln(\delta\omega)$ vs. $1/T$ should be linear, with slope E_a/k. This was indeed found to be the case, thus supporting the hindered rotational model. A least-squares fitting of the plot yielded $E_a = 6.3 \pm 1$ kcal/mol. This value is in agreement with that (~7 kcal/mol) determined by Heidberg et al.[9] for the picryl ring motion in the parent hydrazine (when account is taken of the stabilization due to the hydrogen bonding) and 5 ± 0.2 kcal/mol for DPPH as determined[5] via proton ENDOR.

The present work establishes the following: (a) FT NMR can be used to measure small (≤1 G) ^{14}N hf couplings. (b) The unexpectedly large ^{14}N NMR line widths observed earlier[8] were due to the hindered motion of the picryl ring, with an activation energy of 6.3 ± 1 kcal/mol. (c) Whereas fast relaxation reduces the effectiveness of the EPR/ENDOR/TRIPLE resonance techniques, it helps FT NMR. (d) The available models[10–12] of spin distribution and hf splittings in large organic radicals do not accurately predict nitrogen couplings, and the present results can form a basis for further improvement. We envisage applications of this technique to large biological systems where long-range ^{14}N hf couplings are often expected.

Acknowledgment. This research was supported in part by a grant from the West Virginia University Energy Research Center.

Registry No. 2,2-Diphenyl-1-picrylhydrazyl, 1898-66-4.

---

(10) V. A. Gubanov and A. K. Chirkov, *Acta Phys. Pol. A*, **43**, 361 (1963) and their preceding papers.

(11) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

(12) D. N. Nanda, J. Subramanian, and P. T. Narashimhan, *Theor. Chim. Acta*, **22**, 369 (1971).

(13) Z. Haniotis and H. H. Gunthard, *Helv. Chim. Acta*, **51**, 561 (1968).

(14) V. A. Gubanov, V. I. Koryakov, and A. K. Chirkov, *J. Magn. Reson.*, **11**, 326 (1973).

(15) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, 1967, Chapter 12.

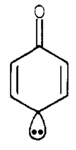
Isomeric σ and π Radicals from Carboxylic Acids and Amides

Michael J. S. Dewar,* Ali H. Pakiari, and
Adriana B. Pierini[1]

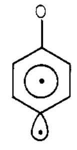
Department of Chemistry
The University of Texas at Austin, Austin, Texas 78712

Received August 10, 1981

The possibility of orbital isomerism[2] in conjugated systems where one conjugated atom has a lone pair of electrons seems to have first been pointed out by Dewar and Narayansawami[3] in the case of the carbene **1**. Excitation of a lone-pair electron into an empty π MO normally gives rise to n→π* excited state (cf. A → B in Figure 1) but if the π LUMO is a bonding or nonbonding MO of low energy and if the "excited state" (cf. **2**) differs from the "ground state" in geometry, the two states may correspond to different local minima on the potential surface separated by an energy barrier (cf. A → C → D in Figure 1). Note that **1** and **2** are distinct isomers because their wave functions differ in symmetry, that of **1** being symmetric and that of **2** antisymmetric, for reflection in the π nodal plane.



1



2

Analogous orbital isomerism is clearly possible in conjugated radicals where the unpaired electron can occupy either of two MOs of comparable energy, one σ and one π, the two MOs containing one or three electrons between them. Radicals of this type derived from amides, imides, or carboxylic acids by loss of a hydrogen atom, e.g., **3–5**, play an important role in various reactions, and their structures have been the subject of much recent work.[4–9]

$RCO\dot{N}H$	$(RCO)_2N\cdot$	$RCOO\cdot$
3a, R = H	**4a**, R = H	**5a**, R = H
b, R = CH_3	b, R = CH_3	b, R = Ph
c, R = CF_3	c, R = CF_3	c, R = CH_3
		d, R = CF_3

---

(1) Grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Cientificas y Tecnicas, Argentina.

(2) Orbital isomers are defined as species distinguishable by different occupation of a set of available MOs. The MOs may be distinguished by symmetry, as here, or by their nodal properties. See: Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *J. Am. Chem. Soc.* **1974**, *96*, 5242.

(3) Dewar, M. J. S.; Narayanaswami, K. *J. Am. Chem. Soc.* **1964**, *86*, 2422.

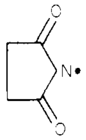
(4) (a) Day, J. C.; Katsaros, M. G.; Kocher, W. D.; Scott, A. E.; Skell, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 1951. (b) Skell, P. S., personal communication.

0002-7863/82/1504-3242$01.25/0

Evidence from ESR spectroscopy seems to have established[7] a π-radical structure for the species derived from amides or imides and ab initio calculations[8,9] support this conclusion in the case of the radicals derived from formamide (**3a**) or diformimide (**4a**). Similar calculations,[8] however, imply that formyl radical (**5a**) should also be most stable in the π form whereas a recent ESR study[10] of benzoyloxy radical (**5b**) seems to have established that it is in fact a σ radical, not a π one.

Baird and Taylor[8] carried out calculations for **3a** and **5a** using the STO-3G and 4-31G basis sets. The π,σ separations found in this way for **3a** were 4.8 and 6.7 kcal/mol, and for **5a** 2.8 and 1.4 kcal/mol, respectively. Use of the larger basis set thus leads to a larger value for **3a** but a smaller one for **5a**. Since the 4-31G separation for **5a** is so small, it seems likely that use of a larger basis set would make the σ isomer the more stable.

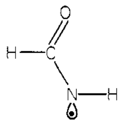
Skell et al.[4] have presented strong chemical evidence for the existence of the succinimidyl radical (**6**) in two isomeric forms, the lower in energy being the π radical and the other the σ radical (which in effect is a $\pi \rightarrow \sigma$ excited state of the π radical). They estimated the difference in energy between them to be ca. 15 kcal/mol. Skell and May[5] have found evidence for similar isomerism in the acetoxy radical (**5c**). This had not previously been observed to abstract hydrogen from other molecules, undergoing decarboxylation exclusively, but photolysis of acetyl hypobromite (**7**) produced it in an excited form which did abstract hydrogen. Since decarboxylation of the σ radical is a symmetry-allowed process while that of the π radical is symmetry forbidden, it seems clear that the normal form of **5c** must be the σ radical and the species generated from **7** the π one.



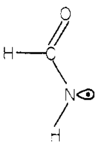
6

CH_3COOBr

7



8



9

Mechanism of reactions cannot in general be studied effectively by ab initio procedures at present because the cost of calculating potential surfaces adequately by methods of adequate accuracy becomes excessive for any but the simplest molecules. For chemical purposes one needs to calculate the systems of specific interest rather than simple models. This difficulty has been met by the parametric methods developed here (MINDO/3,[11] MNDO[12]), which in their regions of applicability seem[13] to be at least equal in accuracy to rather good ab initio calculations and far superior to ones using minimum basis sets (e.g., STO-3G). Extensive tests[11,12,14] have shown them to be applicable to radicals in general and to radical reactions in particular.[15] We have therefore carried out MNDO calculations for various radicals of the type indicated above.

The calculations were carried out with the spin-unrestricted version (UMNDO) of MNDO, with full geometry optimization.[12,16] The standard UMNDO procedure led in each case to the most stable form (σ or π) of each radical. The less-stable form was found by starting with a bond-order matrix derived from that for the corresponding anion (e.g., $RCONH^-$) by removing the contribution of an electron in an occupied MO of the required type. Curiously, removal from the highest such MO often failed to give the required species, but the less stable isomer could then be found by taking a lower lying MO. In acetic acid derivatives, the conformation of methyl was usually chosen to preserve the π nodal plane of symmetry. Again, curiously, in the case of CF_3COO, the π isomer could be found only if the CF_3 group was rotated so that the molecule had a plane of symmetry orthogonal to the π nodal plane. The heats of formation calculated for the various species are shown in Table I and relevant geometrical parameters in Table II. Calculations were included for H_2N since there is an experimental value for the σ–π separation in it (29–32 kcal/mol).[18] Our calculated value suggests that MNDO may overestimate the stabilities of π radicals. Calculations were also carried out for both conformers (**8** and **9**) of HCONH. Since the results were similar (Table I, II), calculations for other amides were confined to species analogous to **8**. Tables I and II also show results for the corresponding anions, which were obtained as byproducts.

As Table I shows, MNDO predicts amido and imido radicals to be most stable in the π form, in agreement with the calculations[8,9] referred to above and the ESR evidence.[7] The π,σ separations are larger than the ab initio one for **3a**. As indicated above, the latter is probably too small. The MNDO separation for **6** agrees nicely with the estimate by Skell et al.[4]

However, MNDO predicts the acyloxy radicals **5a**, **5c**, and **5d** to be σ radicals, in agreement with experiment for **5c** but in contrast to the ab initio calculations for **5a**. As noted above, the discrepancy might be resolved by use of a larger basis set.

Initial calculations for benzoyloxy radical (**5b**) predicted this also to be of σ type with a σ,π separation similar to those for **5a**, **5c**, and **5d** (see Tables). However both radicals were predicted to be nonplanar, which is almost certainly not the case. The error is not surprising because the known[19] tendency of MNDO to overestimate nonbonded repulsions should lead to overestimation of those between the oxygen and the ortho-hydrogen atoms in **5b**, thus tending to twist the COO group out of planarity with the ring. This error should, however, apply equally to both forms of **5b**, so MNDO should reproduce the relative energies of the planar species correctly. When planarity was enforced, both forms were found to have almost identical energies (Table I). Evidently the conjugative interaction between the carboxyl group and the ring stabilizes the π isomer more than the σ isomer, as indeed would be expected[20] from PMO theory, and the difference should of course be reduced by twisting the carboxyl out of planarity with the ring. While it is impossible to draw exact conclusions from MNDO calculations, the π isomer of **5b** is clearly more stable than in the case of the other carboxyl radicals studied, and all three isomers of **5b** (the two mirror-image σ isomers and the π isomer) may well have almost identical energies, as MNDO predicts.

The ESR data for **5b** indicate[10] it to be a σ radical, but they also show that the unpaired electron in it is coupled equally to both oxygen nuclei. If a single species were involved, the CO bond lengths in it would then have to be equal. However, *all* the theoretical calculations agree in predicting the CO bond lengths

---

(5) Skell, P. S.; May, D. D. *J. Am. Chem. Soc.* **1981**, *103*, 967.

(6) (a) Davies, A. G.; Roberts, B. P.; Smith, T. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2221. (b) Chalfont, G. R.; Perkins, M. T. *J. Chem. Soc. B* **1970**, 401. (c) Hedaya, E.; Hinman, R. L.; Schomaker, V.; Theodoropulos, S.; Kyle, L. M. *J. Am. Chem.* **1967**, *89*, 4875.

(7) Lessard, J.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 3262.

(8) Baird, N. C.; Taylor, K. F. *Can. J. Chem.* **1980**, *58*, 753.

(9) Apeloig, Y.; Schreiber, R. *J. Am. Chem. Soc.* **1980**, *102*, 6144.

(10) McBride, J. M.; Merrill, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1723.

(11) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1302, 1307.

(12) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(13) (a) Halgren, T. A.; Kleier, D. A.; Hall, J. H., Jr.; Brown, L. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6595. (b) Dewar, M. J. S.; Ford, G. P. *Ibid.* **1979**, *101*, 5558.

(14) Dewar, M. J. S.; Olivella, S. *J. Chem. Soc., Faraday Trans. 2* **1979**, 829.

(15) Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* **1978**, *100*, 5290. *Ibid*, **1977**, 101, 4958.

(16) Using the Davidon–Fletcher–Powell method; see ref 10. Convergence was checked by calculating and diagonalizing the Hessian (force constant) matrix in Cartesian coordinates and establishing that it had six vanishing eigenvalues.[17]

(17) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625. Komornicki, A.; McIver, J. W., Jr. *Ibid.* **1973**, *95*, 4512. Murrell, J. N.; Laidler, K. J. *Trans. Faraday Soc.* **1968**, *64*, 371.

(18) Adom, W. *Acc. Chem. Res.* **1979**, 390.

(19) As indicated, e.g., by the large positive errors in heats of formation calculated for crowded molecules; see ref 12.

(20) The $-COO(\pi\cdot)$ group is of *E* type, whereas $-COO(\sigma\cdot)$ contains a neutralized system similar to that in the analogous $-COOH$; see ref 21.

(21) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3350. Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; p 420.

Table I. MNDO Calculated Heat of Formation (kcal/mol) for Anions, σ and π Radicals

compd	anion	σ	π	E (π-σ)
NH_2	47.32	76.60	36.51	-40.11
HN_2 (MINDO/3)	56.44	53.36	29.06	-24.30
3a	-44.28	18.53	3.38	-15.15
3b	-52.21	10.37	-4.84	-13.17
3c	-217.79	-124.11	-140.74	-16.63
4a	-97.74	-19.96	-22.67	-2.71
5a	-101.72	-35.16	-30.83	4.33
5b		-9.36	-9.42	0.6
5b (nonplanar)		-13.00	-9.23	-3.77
5c	-110.12	-44.01	-40.15	3.85
5d	-280.54	-179.58	-177.75	1.83
6	-113.07	-23.71	-38.26	-14.55
pyrrole	14.27	97.13	55.85	-41.28

Table II. MNDO Calculated Geometries for Anions and σ and π Radicals

		N-H	C-O	C-N	OCO	NCO	CNC	HNC
HN_2	anion	0.98						
	σ	0.97						
	π	1.00						
NH_2	MINDO/3							
	anion	1.07						
	σ	0.98						
	π	1.04						
3a	anion	1.01	1.26	1.33		128.7		112.4
	σ	1.01	1.33	1.29		125.8		115.9
	π	1.01	1.23	1.41		122.9		113.1
3b	anion	1.01	1.27	1.34		126.16		112.0
	σ	1.01	1.33	1.30		122.90		115.4
	π	1.00	1.24	1.42		120.61		112.7
3c	anion	1.00	1.24	1.32				114.6
	σ	1.00	1.33	1.29				115.6
	π	1.00	1.23	1.40				113.4
4a	anion	1.13	1.24	1.37		122.5	119.0	
	σ	1.11	1.22	1.38		122.1	151.4	
	π	1.11	1.22	1.43		120.2	108.4	
			1.28					
5a	anion		1.26		125.6			
			1.26					
	σ		1.23		120.3			
			1.33					
	π		1.28		118.4			
			1.28					
5b	σ		1.23		127.5			
	(planar)		1.34					
	π		1.26		115.3			
	(planar)							
	σ		1.23		118.7			
			1.33					
	π		1.26		117.1			
			1.26					
5c	anion		1.26		123.6			
			1.26					
	σ		1.34		117.8			
			1.23					
	π		1.29		117.4			
			1.29					
5d	anion		1.24		130.9			
			1.24					
	σ		1.33		124.5			
			1.22					
	π		1.28		120.4			
6	anion	1.11	1.24	1.34		124.6	109.4	
	σ	1.11	1.21	1.39		109.4	120.0	
	π	1.11	1.22	1.43		120.2	108.4	
pyrrole	anion			1.37				105.5
	σ			1.37				117.0
	π			1.37				105.6

in σ acyloxy radicals to be unequal, like those in the carboxylic acids from which they are derived (cf. Table II). The conclusion that **5b** is a σ radical with equal CO bond lengths is therefore difficult to accept. Our calculations seem to provide a possible solution of this problem. If the difference in energy between the σ and π forms of **5b** is indeed negligible, interconversion of the two mirror-image forms of the σ radical via the σ radical may be fast on the ESR time scale, leading to time-averaged equivalence of the oxygen atoms.

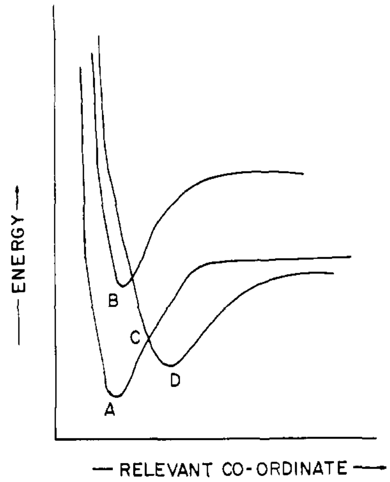


Figure 1. A → B represents a normal $\sigma \rightarrow \pi^*$ transition. If the transition energy is low and the geometry of the "excited" structure D differs sufficiently from that of A, D may represent a local minimum on the *ground-state* surface, separated from A by a barrier (C).

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 79-0008) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out with the Dual Cyber 170/150 computer at the University of Texas Computation Center.

Registry No. 3a anion, 67131-48-0; **3a** radical, 14753-22-1; **3b** anion, 63285-19-8; **3b** radical, 7065-76-1; **3c** anion, 81583-99-5; **3c** radical, 81602-55-3; **4a** anion, 81584-00-1; **4a** radical, 75090-36-7; **5a** anion, 71-47-6; **5a** radical, 16499-21-1; **5b** anion, 766-76-7; **5b** radical, 1854-28-0; **5c** anion, 71-50-1; **5c** radical, 13799-69-4; **5d** anion, 14477-72-6; **5d** radical, 16040-26-9; **6** anion, 28627-67-0; **6** radical, 24344-83-0; NH_2 anion, 17655-31-1; NH_2 radical, 13770-40-6; HN_2 anion, 71004-29-0; HN_2 radical, 36882-13-0; pyrrole anion, 23303-09-5; pyrrole radical, 81584-01-2.

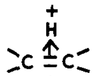
Tritium Migration in Tritiated Anisole

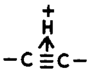
Michael J. S. Dewar* and Charles H. Reynolds

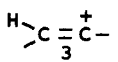
Department of Chemistry
The University of Texas at Austin, Austin, Texas 78712

Received September 21, 1981

1,2 Wagner–Meerwein hydrogen shifts take place with extreme ease, due to the stability of the intermediate π complex[1] (**1**).


1


2


3

Recent MINDO/3[2] and "state-of-the-art" ab initio[3] calculations and experimental studies[4] have indeed indicated that the π com-

---

[1] (a) Dewar, M. J. S. *J. Chem. Soc.* **1946**, 406; Bull. *Soc. Chim. Fr.* **1951**, *18*, c 71; "The Electronic Theory of Organic Chemistry"; Clarendon Press; Oxford, 1949. (b) Dewar, M. J. S.; Marchand, A. P. *Ann. Rev. Phys. Chem.* **1965**, *16*, 321.

[2] Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 7432.

[3] (a) Koehler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1978**, *100*, 5297; **1979**, *101*, 3479.

[4] Dannenberg, J. P.; Goldberg, B. P.; Barton, J. K.; Dill K.; Weinwurzel, D. H.; Longas, M. O. *J. Am. Chem. Soc.* **1981**, *103*, 7764.

0002-7863/82/1504-3244$01.25/0 © 1982 American Chemical Society