39 mg (85%) of a light yellow oil. It was found from its NMR spectrum that the oily residue consisted almost entirely of one component, the epimer of **8a**, *syn*-3,4-benzobicyclo[4.1.0]hept-3-en-2-ol (**12a**): IR (neat) 3350 (OH), 1030, 980, 740 cm^{-1}; NMR is shown in Table I.

The other esters (**1b** and **1c**) were solvolyzed by the method similar to that used in solvolysis of **1a** and the product distribution was determined by the NMR spectrum and its integral intensity for α hydrogen or vinyl hydrogen. The results was shown in Table IV. The NMR spectrum of the epimer of **8b** was assumed from that of products **12b** and **13b**. NMR spectrum for **12b** ($CDCl_3$): δ 7.12 (s, 4 H, aromatic), 5.00 (d, J = 3 Hz, 1 H, α hydrogen), 3.20 and 2.88 (ABq, J = 16 Hz, 2 H, benzyl), 1.30 (s, 3 H, methyl), 1.48–0 (m, 3 H, cyclopropyl), and the other signals.

A mixture containing 100 mg of **8b** (0.58 mmol), 300 mg (2.9 mmol) of 2.6-lutidine, and 100 mg (0.6 mmol) of p-nitrobenzoic acid in 100 mL of 80% aqueous acetone was heated at 45 °C for 1 day. After usual workup, 93 mg of colorless solid was obtained. A comparison of the NMR spectrum before and after heating showed that **8b** was stable to the reaction conditions. Similar treatment of **8a** and **8c** gave the same results.

Acknowledgments. This work was partly supported by a grant from the Ministry of Education of Japan, No. 874145, in 1973.

Registry No.—*cis*-**2b**, 64425-83-8; *trans*-**2b**, 64414-48-8; **2c**, 64425-29-2; **3b**, 64414-49-9; **3c**, 64414-50-2; *cis*-**4b**, 64414-51-3; *trans*-**4b**, 64414-52-4; **4c**, 64414-53-5; **5b**, 64414-54-6; **5c**, 64414-55-7; **6b**, 64414-56-8; **6c**, 64414-36-4; **7a**, 27346-16-3; **7b**, 64414-46-6; **7c**, 64414-47-7; **9**, 7148-59-6; **11b**, 29840-37-7; **11c**, 64414-37-5; **13b**, 64414-38-6; **13c**, 64414-39-7; 2-benzyl-2-methylsuccinic acid, 32980-47-5; p-toluenesulfonyl chloride, 98-59-9; p-nitrobenzoyl chloride, 122-04-3; p-nitrobenzoic acid, 62-23-7; 2,6-lutidine, 108-48-5.

Supplementary Material Available: infrared and proton NMR data for **1a–c** and **7a–c** (Table V) (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For major reviews, see: (a) M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **7**, 577 (1968); (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1969, p 1295.

(2) (a) N. A. Clinton, R. S. Brown, and T. G. Traylar, *J. Am. Chem. Soc.*, **92**, 5228 (1970); (b) R. S. Brown and T. G. Traylor, *ibid.*, **95**, 8025 (1973); (c) C. F. Wilcox, Jr., and H. D. Banks, *ibid.*, **94**, 8232 (1972); (d) C. F. Wilcox, L. M. Loew, and R. Hoffmann, *ibid.*, **95**, 8192 (1973); (e) H. C. Brown and E. N. Peters, *ibid.*, **95**, 2400 (1973); (f) G. A. Olah and P. W. Westerman, *ibid.*, **95**, 7530 (1973); (g) D. F. Eaton and T. G. Traylor, *ibid.*, **96**, 1226 (1974); (h) G. A. Olah, P. W. Westerman, and J. Nishimura, *ibid.*, **96**, 3548 (1974); (i) J. F. Wolf, P. G. Harch, R. W. Taft, and W. J. Hehre, *ibid.*, **97**, 2902 (1975); (j) H. Volz, J. Shin, and H. Streicher, *Tetrahedron Lett.*, 1297 (1975); (k) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **99**, 1712 (1977); (l) H. C. Brown, M. Ravindranathan, and E. N. Peters, *J. Org. Chem.*, **42**, 1073 (1977); (m) H. C. Brown, E. N. Peters, and M. Rabindranathan, *J. Am. Chem. Soc.*, **99**, 505 (1977).

(3) (a) K. Ohkata, *Bull. Chem. Soc. Jpn.*, **49**, 235 (1976); (b) K. Ohkata, *J. Org. Chem.*, **41**, 2162 (1976).

(4) S. Julia and Y. Bonnet, *Bull. Soc. Chim. Fr.*, 1340 (1957).

(5) A. Foncaud, *C. R. Hebd. Seances Acad. Sci.*, **251**, 2975 (1960).

(6) (a) C. C. Hinckley, *J. Am. Chem. Soc.*, **91**, 5160 (1969); (b) C. C. Hinckley and W. C. Brumley, *ibid.*, **98**, 1331 (1976).

(7) (a) G. E. Hawkes, D. Leibfrity, D. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, **95**, 1659 (1973); (b) H. Dürr and W. Bujnoch, *Justus Liebigs Ann. Chem.*, 1691 (1973); (c) O. Hofer, *Tetrahedron Lett.*, 3415 (1975); (d) K. L. Servis, D. J. Bowler, and C. Iahii, *J. Am. Chem. Soc.*, **98**, 73 (1976); (e) D. S. Crumrine and H. B. Yen, *J. Org. Chem.*, **41**, 1273 (1976).

(8) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Am. Chem. Soc.*, **92**, 5734 (1970).

(9) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(10) G. R. Sullivan, *J. Am. Chem. Soc.*, **98**, 7162 (1976).

(11) C. D. Poulter, R. S. Boikess, J. I. Brauman, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2291 (1972), and references cited therein.

(12) J. Tadanier and W. Cole, *J. Org. Chem.*, **27**, 4610 (1962); G. Bauslaugh, G. Just, and E. Lee-Ruff, *Can. J. Chem.*, **44**, 2837 (1966).

(13) Structural assignment in some bicyclic cyclopropylmethyl systems has been made by comparing these reactivities. (a) Methylenation (Simmons-Smith reaction) of cyclic allylic alcohols: C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Am. Chem. Soc.*, **91**, 6892 (1969). (b) Reduction of cyclopropyl ketone with hydride reagents: C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **92**, 4274 (1970). (c) Solvolysis rate of cyclopropylmethyl esters: L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 2316 (1966); P. G. Gassman, R. N. Steppel, and E. A. Aromour, *Tetrahedron Lett.*, 3287 (1973).

(14) P. v. R. Schleyer and G. W. Van Deiene, *J. Am. Chem. Soc.*, **88**, 2321 (1966).

(15) The NMR spectrum of **12b** was expected from that of a mixture of **12b** and **13b**.

(16) L. E. Friedrich and G. B. Schuster, *Tetrahedron Lett.*, 3171 (1971). K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1969, p 1313, and references cited therein.

(17) A. C. Cope and C. M. Hofmann, *J. Am. Chem. Soc.*, **63**, 3452 (1941).

(18) A. Foucaud, *Bull. Soc. Chim. Fr.*, 579 (1964).

(19) See paragraph at end of paper concerning supplementary material.

A Carbon-13 Nuclear Magnetic Resonance Investigation of Substituted 4-X-2,6-Dinitroanisoles and Related Meisenheimer 1,1-Complexes

Marie-Paule Simonnin,[1a] Marie-José Pouet,[1a] and François Terrier*[1a,b]

Laboratoires de spectrographie (ERA CNRS 390) et de physicochimie des solutions (LA CNRS 161), ENSCP, 75231-Paris, Cédex 05, and Département de Chimie, Faculté des Sciences de Rôuen, 76130-Mont Saint Aignan, France

Received July 11, 1977

Carbon-13 NMR chemical shifts for various substituted 4-X-2,6-dinitroanisoles 1 (X = SO_2CF_3, NO_2, CN, SO_2CH_3, COC_6H_5, CF_3, Cl, H) and related *gem*-dimethoxyl adducts **2** (X = SO_2CF_3, NO_2, CN, SO_2CH_3, COC_6H_5, CF_3) are reported. In the case of anisoles 1 the deviations from additivity of substituent effects observed for $C_{2,6}$ and C_1 together with the absence of a deshielding of C_4 indicate an inhibition of resonance of the *o*-nitro groups. Good linear correlations with the Swain and Lupton reactivity parameters are observed for δ_{C_1}, ${}^1J_{^{13}C_7H}$, ${}^1J_{C_3H_3}$ in these tetrasubstituted benzenes. ^{13}C chemical shifts measured for adducts **2** reveal an increase in the negative charge located at $C_{2,6}$ and C_4, but a decrease at $C_{3,5}$, in agreement with SCFMO calculations. However, no relation exists between these shifts and the known thermodynamic stability of adducts **2**.

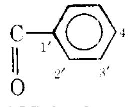
The reaction of methoxide ions with substituted 4-X-2,6-dinitroanisoles 1 usually gives the *gem*-dimethoxyl 1,1-complexes 2 as the stable products.[2] From thermodynamic and kinetic studies on the one hand[2–6] and crystallographic and ^1H NMR studies on the other hand,[2–7,11] it appears that the electron-withdrawing ability of the ring substituents and the release of steric compression which exists between the methoxyl group and the adjacent nitro groups in the parent ethers 1 are two major factors responsible for the stability of complexes **2**. Since they are known to depend on steric and charge distribution effects, ^{13}C chemical shifts could be reasonably expected to yield further information on both of these

0022-3263/78/1943-0855$01.00/0 © 1978 American Chemical Society

Table I. ^{13}C Chemical Shifts of 4-X-2,6-Dinitroanisoles 1 in Me_2SO-d_6 with Me_4Si as Internal Standard

X	Registry no.	δ_{C_1}	δ_{C_2}	δ_{C_3}	δ_{C_4}	δ_{C_7}	δ_X	$^1J_{C_7H}$	$^1J_{C_3H_3}$	$^3J_{C_3H_5}$	$^2J_{C_4H_3}$	Other coupling const
H	3535-67-9	146.2_5	144.5_6	129.6_5	125.0_5	64.3_5						
Cl	6302-58-5	145.1_6	144.9_1	129.3_2	128.2_4	64.5_2		148.9	176	6.0_5	5.1_5	
CF_3	317-70-4	149.2_3	144.8_1	126.8_6	124.6_0	64.5_9	122.1_2	149.7	173.8			$^1J_{C_XF} = 272.8$ $^2J_{C_4F} = 35.4$ $^3J_{C_3F} = 3.6$
CN	19018-96-3	149.7_3	144.3_9	133.6_1	107.0_3	64.5_6	115.3_7	149.7	177	7.4	1.9_5	$^3J_{C_XH_3} = 5.4$
SO_2CH_3	39880-50-7	150.1_0	144.1_8	128.4_9	135.8_8	64.5_8	43.0_2	149.9	175.5	6.9_5		
$CO—C_6H_5$	39880-47-2	149.0_4	144.0_4	130.1_1	132.4_6	64.4_8	*a*	149.6	172.2	7.6_5	1.2	$^2J_{C_2H_3} = 2.5_5$
NO_2	606-35-9	150.8_3	143.8_7	124.6_0	141.4_4	64.8_0		150.1	177.9	5.5		
SO_2CF_3	19822-29-8	153.1_1	144.9_3	131.5_6	124.0_6	64.8_1	119.1_9	150.5	177.8			$^1J_{C_XF} = 325.6$

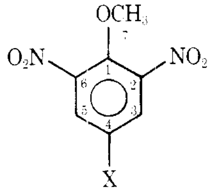
[a] X =



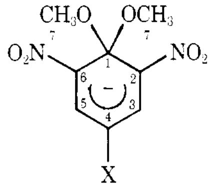
$\delta_{C_{1'}} = 135.1_9$, $\delta_{C_{2'}} = 129.8_9$, $\delta_{C_{3'}} = 128.8_1$, $\delta_{C_{4'}} = 133.6_4$, $\delta_{CO} = 191.2_8$.

factors. Following a previous ^{1}H NMR study[11], we have therefore performed a ^{13}C NMR spectroscopic study of anisoles 1 and 1,1-complexes 2.

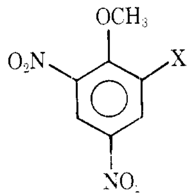
During the course of our work, Olah and Mayr published a paper in which they reported a similar investigation of isomeric 2-X-4,6-dinitroanisoles 3 and corresponding 1,1-complexes 4.[12] The constancy of the steric strain in our anisoles 1 allows, however, a more precise structural analysis.



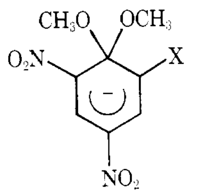
1



2



3



4

Results

Because of the symmetrical structures of anisoles 1 and complexes 2, ^{13}C NMR spectra showed four signals for the ring carbons and one signal for the methoxyl carbon(s). Other absorptions were observed for carbons belonging to the X substituent. Assignments were deduced from proton-coupled spectra and intensity arguments.

Substituted Anisoles 1. The high-field absorption ($\simeq$64.5 ppm) which gave a quartet in the proton-coupled spectra ($^1J_{C_7H} \simeq 150$ Hz) was unambiguously assigned to the methoxyl C_7 carbon. C_1, whose resonance was observed at low field (145–153 ppm), appeared as a poorly resolved multiplet in the proton-coupled spectra. This unresolved fine structure suggests that C_1 is spin coupled through three bonds to the three protons of the OCH_3 group and the two protons H_3 and H_5.

The shielding of carbons $C_{2,6}$ was expected to be only slightly affected by the X substituent which is located in a meta position. Their resonance appeared in a narrow range around 144 ppm. Furthermore, these carbons have neither $^1J_{CH}$ nor $^3J_{CH}$ but only $^2J_{CH}$ and $^4J_{CH}$ coupling constants which are known to be small. In the proton coupled spectra, they gave a broad signal, which is probably due to the effect of the adjacent ^{14}N nucleus.

In the proton-decoupled spectra, the signal belonging to carbons $C_{3,5}$ was very intense because of the nuclear Overhauser effect. This signal became a double doublet in the proton-coupled spectra due to the $^1J_{CH}$ and $^3J_{CH}$ coupling constants. For X = CF_3, the $C_{3,5}$ resonance was a quartet showing a $^3J_{CF}$ coupling constant ($^3J_{C_3F} = 3.6$ Hz).

As expected, C_4 which is directly attached to the X substituent had the most affected shielding; its shift covers a wide range (107–141 ppm). When X = CF_3, this signal was a quartet ($^2J_{C_4F} = 35.4$ Hz). In the proton-coupled spectra, the C_4 resonance was the X part of an A_2X system and gave a triplet ($^2J_{C_4H} = 1$–5 Hz).

Finally, these assignments were confirmed by the use of additivity of substituent effects when these effects were known (vide infra). The results are summarized in Table I.

Anionic Complexes 2. The intense signal at ca. 52 ppm was assigned to the methoxyl carbons C_7; this assignment was confirmed by selective irradiation of the corresponding methoxyl protons.

The resonance of the sp^3 carbon C_1 was observed around 102–104 ppm. In the proton-coupled spectra, it was a poorly resolved multiplet (compare C_1 in the parent anisoles). The low-field absorptions (126–136 ppm) were assigned to $C_{2,6}$ and $C_{3,5}$ respectively as follows. In the proton-coupled spectra, each of these carbons appears as the X part of an ABX system where $\nu_A - \nu_B$ is very small since it corresponds to a ^{13}C isotope effect.[13,23] In the case of $C_{3,5}$ the magnitudes of J_{AX} and J_{BX} are quite different, since these coupling constants are $^1J_{CH}$ and $^3J_{CH}$, respectively, and these carbons gave a double doublet. On the other hand, in the case of $C_{2,6}$, both J_{AX} and J_{BX} are small (as expected for $^2J_{CH}$ and $^4J_{CH}$ coupling constants), and the resonance of these carbons was a 1:1:1 triplet; the separation of the outer lines gave the sum $|^2J_{CH} + {}^4J_{CH}|$. Proton-coupled spectra also allowed an unambiguous assignment of the C_4 resonance, which appeared as the X part of an A_2X system and gave a 1:2:1 triplet.

When X = SO_2CF_3, a quartet was observed for the carbon resonance of the trifluoromethyl group ($^1J_{CF} = 326.2$) and a small coupling through three bonds ($^3J_{C_4F} = 2$ Hz) was resolved in the C_4 signal. C–F coupling constants through one, two, and three bonds were also observed for X = CF_3. The results are summarized in Table II.

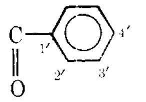
Discussion

Substituted Anisoles. (1) Additivity of Substituent Effects. Conformational Features. The ^{13}C chemical shifts

Table II. ^{13}C Chemical Shifts of 1,1-Dimethoxy-2,6-dinitro-4-X-cyclohexadienate Anions 2 in Me_2SO-d_6 with Me_4Si as Internal Standard

X	Registry no.	δ_{C_1}	δ_{C_2}	δ_{C_3}	δ_{C_4}	δ_{C_7}	δ_X	$^1J_{C_7H}$	$^1J_{C_3H_3}$	$^3J_{C_3H_5}$	$\Sigma\|J_{C_2H_3} + {}^4J_{C_2H_5}\|$	Other coupling const
CF_3	28933-97-3	104.5_0	126.3_3	131.6_6	94.3_7	51.9_5	125.4_1	142.5				$^1J_{CF} = 268.0$ $^2J_{C_4F} = 34.6$ $^3J_{C_3F} = 3.1$
CN	25549-13-7	102.7_4	127.8_7	136.3_7	73.6_8	51.9_3	120.9_1	142.6	163	7.2	5.7	$^3J_{C_XH_3} = 4.7$
SO_2CH_3	40203-26-7	103.0_5	126.7_9	132.6_9	103.7_9	51.9_0	44.6_1	142.3	162.7	6.5	5.6	
$CO-C_6H_5$	40203-23-4	102.6_6	128.4_4	135.7_1	104.2_1	51.8_8	*a*	142.5	159.4	7.3	5.5	
NO_2	12128-30-2	102.0_5	128.6_4	128.9_0	117.4_1	52.1_1	—	143.5	165.5	5.2	6.3	$^2J_{C_4H_3} = 3.7$
SO_2CF_3	35298-04-5	102.1_1	128.9_2	133.0_5	87.8_0	52.1_9	120.3_1	143.2	164.5	6.4	6.2	$^1J_{CF} = 326.2$ $^3J_{C_4F} \simeq {}^2J_{C_4H_3} \simeq 2$

[a] X =



$\delta_{CO} = 189.6_5$, $\delta_{C_{1'}} = 139.5_9$, $\delta_{C_{2'}} = 128.0_6$, $\delta_{C_{3'}} = 128.0_6$, $\delta_{C_{4'}} = 130.1_6$.

Table III. Observed and Predicted Aryl Carbon Shieldings Relative to Benzene for 4-X-2,6-Dinitroanisoles 1

	$\Delta\delta_{exptl}$				$\Delta\delta_{calcd}$[a]				$\Delta\delta_{calcd} - \Delta\delta_{exptl}$			
X	C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4
H	17.7_5	16.0_6	1.1_5	-3.4_5	21.8	6.5	2.0	−5.9	4.0_5	-9.5_6	0.8_5	-2.4_5
Cl	16.6_6	16.4_1	0.8_2	-0.2_6	19.9	7.8	2.4	0.3	3.2_4	-8.6_1	1.5_8	0.5_6
CF_3 (c)	20.7_3	16.3_1	-1.6_4	-3.9_0	25.0	6.8	−0.2	−14.9	4.2_7	-9.5_1	1.4_4	−11.0
(d)					25.0	6.8	−1.0	−3.1	4.2_7	-9.5_1	0.6_4	0.8_0
CN	21.2_3	15.8_9	5.1_1	-21.4_7	25.7	7.1	5.6	−21.3	4.4_7	-8.7_9	0.4_9	0.1_7
SO_2CH_3	21.6_0	15.6_8	-0.0_1	7.3_8	26.6	7.1	0.5	6.4	5.0	-8.5_8	0.5_1	-0.9_8
COC_6H_5	20.5_4	15.5_4	1.6_1	3.9_6	25.4	6.3	3.7	3.5	4.8_6	-9.2_4	2.0_9	-0.4_6
NO_2	22.3_3	15.3_7	−3.9	12.9_4	27.6	7.4	−2.8	14.1	5.2_7	-7.9_7	1.1	1.1_6

	$\Delta\delta'_{calcd}$[b]				$\Delta\delta'_{calcd} - \Delta\delta_{exptl}$			
X	C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4
H								
Cl	15.8_5	17.3_6	1.5_5	2.7_5	-0.8_1	0.9_5	0.7_3	3.0_1
CF_3 (c)	20.9_5	16.3_6	-1.0_5	-12.4_5	0.2_2	0.0_5	0.5_9	-8.5_5
(d)	20.9_5	16.3_6	-1.8_5	-0.6_5	0.2_2	0.0_5	-0.2_1	3.2_5
CN	21.6_5	16.6_6	4.7_5	-18.8_5	0.4_2	0.7_7	-0.3_6	2.6_2
SO_2CH_3	22.5_5	16.1_2	-0.3_5	8.8_5	0.9_5	0.4_4	-0.3_4	1.4_7
COC_6H_5	21.3_5	15.8_6	2.8_5	5.9_5	0.8_1	0.3_2	1.2_4	1.9_9
NO_2	23.5_5	16.9_6	-3.6_5	16.5_5	1.2_2	1.5_9	0.2_5	3.6_1

[a] $\Delta\delta$ values calculated from benzene. [b] $\Delta\delta'$ values calculated from 2,6-dinitroanisole. [c] Values with increments from ref 15 and 16. [d] Values with increments determined in this work.

of polysubstituted aromatics can be calculated by using the additivity of substituent effects.[14] Provided that the substituents are not ortho to each other, good additivity relationships are usually found, with differences between observed and calculated shifts less than ±2 ppm. In ortho-substituted derivatives, the additivity relation breaks down and ^{13}C shieldings have been shown to reflect the degree of steric hindrance to electronic interactions.[15]

Table III compares the calculated ($\Delta\delta_{calcd}$) and observed ($\Delta\delta_{exptl}$) shifts relative to that of benzene (128.5 ppm). Although substituent effects of monosubstituted benzenes were measured in CCl_4[16,17] or $CDCl_3$[18] and our values in Me_2SO-d_6, the agreement is quite good for C_3 and C_4; the discrepancy observed for C_4 in the case of the trifluoromethyl derivative will be discussed later. In contrast, strong deviations occur for C_1 and C_2. In every case, C_1 is more shielded than expected from the calculations ($\Delta\delta_{calcd} - \Delta\delta_{exptl} \simeq +4$ ppm) whereas an opposite trend is observed for C_2 ($\Delta\delta_{calcd} - \Delta\delta_{exptl} = -9$ ppm). These deviations reflect the existence of a severe steric compression in ortho dinitroanisoles 1, which results in the steric inhibition of resonance of the *o*-nitro groups and not in that of the methoxyl group as was recently concluded by Olah and Mayr.[12]

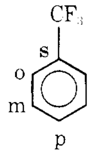
Indeed, a distorted coplanarity of the methoxyl group should result in an attenuation of the conjugative electron release by oxygen and therefore in a deshielding of C_4. Such an effect is, in fact, observed in 2,6-dialkylanisoles[15] where the methoxyl group is known to lie out of the aromatic plane. In contrast, this effect is absent in 2-nitroanisole,[15] 2-X-4,6-dinitroanisoles,[12] and in the 4-X-2,6-dinitroanisoles examined here. We therefore conclude from ^{13}C chemical shifts that the methoxyl groups in anisoles 1 and 3 lie in the aromatic plane, while the adjacent nitro groups are twisted out of this plane. This conclusion is in full agreement with that obtained from ^{1}H NMR studies[11,19] as well as from x-ray data[7] on 2,4,6-trinitrophenetole; in the solid state, dihedral angles of 32 and 61° have been observed between the ring and the nitro groups ortho to the ethoxyl group.

As the X substituent is attached to C_4, it should be emphasized that the geometry of C_1 in all the anisoles 1 must be independent of X. Hence, it was of interest to check further substituent effects by taking into account the distorted geometry of the *o*-nitro groups. Assuming additivity effects from the 4-X substituent, we have recalculated ^{13}C chemical shifts by using the experimental ^{13}C shifts of 2,6-dinitroanisole **1** (X = H) as the reference compound. As can be seen in Table III, excellent agreement is now obtained between the $\Delta\delta'_{calcd}$ and the $\Delta\delta_{exptl}$ values for C_1, $C_{2,6}$, and $C_{3,5}$ ($\Delta\delta'_{calcd} - \Delta\delta_{exptl} < 1.6$ ppm). However, C_4 is more shielded than expected from these calculations and the difference $\Delta\delta'_{calcd} - \Delta\delta_{exptl}$ varies from 2 to 3.6 ppm. Thus, the additivity of substituent effects holds for C_1 and C_2 and C_3 in these tetrasubstituted benzenes when the twisting of the *o*-nitro groups is taken into account but it fails for C_4 which is directly bonded to the X substituent. Similar nonadditive ^{13}C substituent effects have been recently observed in para-disubstituted benzenes.[20]

(2) The Abnormal Behavior of the Trifluoromethyl Derivative. The large deviation observed for C_4 in the trifluoromethyl derivative **1** (X = CF_3) suggested a possible error in the reported ^{13}C chemical shift of trifluoromethylbenzene (**5**).[16,17] A reexamination of the ^{13}C spectrum of **5**, using experimental conditions similar to those previously described,[16] gave the following substituent shifts (relative to internal C_6H_6) and ^{13}C–F coupling constants.

C_s, +2.8	C_o, −3	C_m, +0.3	C_p, +3.2	(in ppm)
$^2J_{CF} = 32.4$	$^3J_{CF} = 3.7$	$^4J_{CF} < 0.4$	$^5J_{CF} = 0.9$	(in Hz)

Comparing with reported data shows that the value for C_s (−9 ppm[16,17]) has to be significantly changed. Indeed, our revised value gives a calculated shift for C_4 which is consistent with experiment (see Table III).



5

(3) Correlation of Substituent Effects with Substituent Parameters. Recent articles have shown that substituent effects can be, in some cases, related to substituent constants by means of a two-parameter equation involving either the Taft or Hammett constants[21-23] or the Swain and Lupton reactivity parameters *F* and *R*.[24-27] Thus, in monosubstituted benzenes, good correlations have been obtained between the ^{13}C shifts of the para carbon and the σ_I, σ_R constants[22] as well as between some $J_{^{13}CH}$ coupling constants and the σ_I, σ_p constants.[23] Similarly, chemical shifts and coupling constants in some substituted heteroaromatic compounds have been found to correlate with *F* and *R*.[24,25]

Since the anisoles **1** are tetrasubstituted compounds, it was of a special interest to look for the existence of such correlations between their ^{13}C shifts or $J_{^{13}CH}$ coupling constants and, for instance, the *F* and *R* parameters of the X substituent. The regression equations $z_k = i_k + f_kF + r_kR$ where z_k is the NMR parameter and f_k and r_k are the regression constants were calculated by a linear least-squares multiple correlation computer program. All substituents were included in the data, except X = SO_2CF_3, for which the *F* and *R* parameters are so far not known.[26,27] Good correlations (c, correlation coefficient; σ, standard deviation) were obtained for δ_{C_1}, $^1J_{^{13}C_7H}$, and $^1J_{C_3H_3}$. The equations are:

$$\delta_{C_1} = (145.88 \pm 0.41) + (2.15 \pm 0.83)F + (11.92 \pm 1.50)R$$
$$c = 0.982, \quad \sigma = 0.475$$

$$^1J_{^{13}C_7H} = (148.74 \pm 0.17) + (0.84 \pm 0.22)F + (2.06 \pm 0.21)R$$
$$c = 0.985, \quad \sigma = 0.109$$

$$^1J_{C_3H_3} = (169.08 \pm 1.36) + (8.94 \pm 1.70)F - (4.87 \pm 2.64)R$$
$$c = 0.952, \quad \sigma = 0.835$$

As expected, the chemical shift of C_1 depends on both inductive and mesomeric effects of the X substituent. The positive signs found for the regression constants indicate that electron-withdrawing groups (−1, −M) give downfield shifts while the two contributions are of opposite signs for the (−I, +M) substituents. In this latter case, upfield shifts can then be observed, which is the case for X = Cl.

The correlation obtained for the $^1J_{^{13}C_7H}$ coupling constant of the methoxyl group indicates that this coupling is weakly affected by inductive and mesomeric effects and it increases when X is electron withdrawing (−I, −M). The regression constants *f* and *r* have opposite signs in the equation for $^1J_{C_3H_3}$. However, the inductive contribution *fF* is greater than the mesomeric one *rR*, so that both (−I, −M) and (−I, +M) substituents tend to increase $^1J_{C_3H_3}$. Although a comparison with monosubstituted benzenes is difficult (the corresponding $J_{^{13}CH}$ values were correlated with the σ_p, σ_I constants), both results suggest that the coupling constants $^1J_{CH}$ in substituted aromatic compounds are dependent on both inductive and mesomeric effects of the substituents.[23]

The lack of correlation between chemical shifts of C_2, C_3, and C_4 with *F* and *R* is in accord with a recent study of Smith and Proulx.[28] These authors have succeeded in correlating ^{13}C, ^{1}H, and ^{19}F chemical shifts in aromatic and olefinic systems with substituent effects by using a three-parameter equation of the type:

$$\delta = aF + bR + cQ + d$$

where *F* and *R* are the Swain and Lupton parameters and *Q* is the semiempirical parameter initially proposed by Schaefer et al. to rationalize the ortho effect.[29] The equations obtained for ^{13}C shifts in aromatic systems show that the absolute value of the *cQ* contribution decreases with increasing the number of bonds between the X substituent and the considered carbon. As a consequence, this factor becomes negligible only for the para carbon, i.e., C_1 in the anisoles **1**.

Anionic Complexes 2. As can be seen in Table II, the ^{13}C shifts in anionic σ complexes **2** are not significantly affected by the X substituent, with the exception of C_4 which is directly bonded to X. On the other hand, the number of complexes is too limited for testing the existence of possible correlations with the *F* and *R* parameters.

Going from anisoles **1** to complexes **2** results in a strong upfield shift of both C_1 and the methoxyl carbon. This is consistent with the change in the hydridization of C_1. Moreover, in agreement with SCFMO calculations[30,31] which predict an increase in the negative charge located at the 2, 4, and 6 positions and a decrease at the 3 and 5 positions, we observed that resonances of $C_{2,6}$ and C_4 move to high field whereas those of $C_{3,5}$ move slightly to low-field.

According to Olah and Mayr,[12] the charge effects would be essentially responsible for the changes in sp^2 carbon shifts between anisoles **1** and complexes **2**. In such an hypothesis, a decrease in the $\Sigma\Delta\delta$ sum of the changes in the ^{13}C shifts of sp^2 carbons should reflect an increase in the electron density of the olefinic carbons in **2** and therefore a parallel decrease in the fraction of the negative charge absorbed by the two nitro groups and the X substituent. As seen in Table IV, the $\Sigma\Delta\delta$ values are decreasing according to the sequence NO_2, COC_6H_5, CF_3, SO_2CH_3, CN, and SO_2CF_3 indicating that the negative charge would be delocalized to the greatest extent in the trinitro compound and to the least extent in the trifluoromethylsulfonyl complex.

Such a result is unexpected and difficult to assess for the following reasons. As previously mentioned, the stability of *gem*-dimethoxyl complexes is mainly dependent on the release

Table IV. Comparison of the Thermodynamic Stability of Adducts 2 with the Differences between Their ^{13}C NMR Shifts and Those of the Parent Anisoles 1

X	$\Delta\delta_{C_2}$	$\Delta\delta_{C_3}$	$\Delta\delta_{C_4}$	$\Sigma\Delta\delta^a$	$K_b{}^b$
CF_3	-18.4_8	$+4.8_0$	-30.2_3	-57.5_9	5
COC_6H_5	-15.6_0	$+5.6_0$	-28.2_5	-48.2_5	45^c
SO_2CH_3	-17.3_9	$+4.2_0$	-32.0_9	-58.4_7	101
CN	-16.5_2	$+2.7_6$	-33.3_5	-60.8_7	168
NO_2	-15.2_3	$+4.3_0$	-24.0_3	-45.8_9	19500
SO_2CF_3	-16.0_1	$+1.4_9$	-36.2_6	-65.3_0	1.2×10^6

[a] $\Sigma\Delta\delta = 2(\Delta\delta_{C_2} + \Delta\delta_{C_3}) + \Delta\delta_{C_4}$. [b] Values at 20 °C, ref 5. [c] F. Terrier, unpublished results.

of steric compression which exists in the parent anisoles and the electron-withdrawing character of the ring substituents. Since the former factor is constant in our series, it would be reasonable that the stability order found experimentally for complexes **2** be parallel to the above $\Sigma\Delta\delta$ sequence. That this conclusion is contradicted by the results is obvious from Table IV where we list the values measured for the equilibrium constants for formation of complexes **2** in methanol. In contrast, the observed stability sequence $SO_2CF_3 > NO_2 > CN \simeq SO_2CH_3 > COC_6H_5 > CF_3$ is entirely consistent with the known electronic effects of the substituents. We therefore conclude that ^{13}C NMR chemical shifts are not simply related to the electron-withdrawing effect of the ring substituents and that due care must be taken in their analysis. A similar situation was, indeed, recently observed by Larsen and Bouis in the case of some benzoyl cations.[32]

Experimental Section

^{13}C NMR spectra were recorded at 25.17 MHz on a Varian XL-100-12 W.G. spectrometer in the Fourier transform mode. The instrument was equipped with a 620 L-100-16 K on-line computer. All spectra were run in dimethyl sulfoxide-d_6 ($c \simeq 0.8$ M) using the solvent ^2H signal for internal field-frequency lock. The temperature of the probe was 31 ± 2 °C.

^{13}C chemical shifts were measured relative to internal Me_4Si using standard conditions of ^1H noise decoupling and spectral width of 5000 Hz (digital resolution: 1.25 Hz/point). C–H and C–F coupling constants were measured using 2500 or 1000 Hz spectral widths (digital resolution: 0.68 or 0.25 Hz/point). Proton coupled ^{13}C spectra were obtained with gated proton decoupling (gated off during the data acquisition time but on during the pulse delay) to retain the nuclear Overhauser signal enhancement[33].

Various substituted 4-X-2,6-dinitroanisoles and related 1,1-complexes were prepared as previously described.[11]

References and Notes

(1) (a) ENSCP, address to which inquiries should be sent; (b) Faculté des Sciences de Rouen.
(2) a) R. Foster and C. A. Fyfe, *Rev. Pure. Appl. Chem.*, **16,** 61 (1966); (b) E. Buncel, A. R. Norris, and K. E. Russel, *Q. Rev., Chem. Soc.*, **22,** 123 (1968); (c) M. R. Crampton, *Adv. Phys. Org. Chem.*, **7,** 211 (1969); (d) M. J. Strauss, *Chem. Rev.*, **70,** 667 (1970); (e) C. F. Bernasconi, *MTP Int. Rev. Sci.: Org. Chem., Ser. One*, **3,** 33 (1973).
(3) C. F. Bernasconi, *J. Am. Chem. Soc.*, **93,** 6975 (1971).
(4) F. Terrier, A. P. Chatrousse, and R. Schaal, *J. Org. Chem.*, **37,** 3010 (1972).
(5) F. Terrier, F. Millot, and J. Morel, *J. Org. Chem.*, **41,** 3892 (1976).
(6) J. H. Fendler, W. L. Hinze, and L. J. Liu, *J. Chem. Soc., Perkin Trans. 2,* 1768 (1975).
(7) C. M. Grammacioli, R. Destro, and M. Simonetta, *Acta. Crystallogr., Sect. B,* **24,** 129 (1968).
(8) H. Ueda, N. Sakabe, and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **41,** 2866 (1968).
(9) K. L. Servis, *J. Am. Chem. Soc.,* **87,** 5495 (1965).
(10) E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, **34,** 689 (1969).
(11) M. P. Simonnin, M. J. Lecourt, F. Terrier, and C. E. Dearing, *Can. J. Chem.*, **50,** 3558 (1972).
(12) G. A. Olah and H. Mayr, *J. Org. Chem.*, **41,** 3448 (1976).
(13) M. Hansen and H. J. Jakobsen, *J. Magn. Reson.*, **20,** 520 (1975).
(14) J. B. Stothers in "Carbon-13 NMR Spectroscopy", A. T. Blomquist and H. Wasserman, Ed., Academic Press, New York, N.Y., 1972, p 201.
(15) G. W. Buchanan, G. Montaudo, and P. Finocchiaro, *Can. J. Chem.*, **52,** 767 (1974).
(16) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, **94,** 3089 (1972).
(17) G. C. Levy and G. L. Nelson, Ed., "Carbon-13 NMR for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 81
(18) G. W. Buchanan, C. Reyes-Zamora, and D. E. Clarke, *Can J. Chem.*, **52,** 3895 (1974).
(19) F. Terrier, J. C. Halle, and M. P. Simonnin, *Org. Magn. Reson.*, **3,** 361 (1971).
(20) J. Bromilow, R. T. C. Brownlee, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, **98,** 2020 (1976).
(21) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10,** 1 (1973).
(22) S. K. Dayal and R. W. Taft, *J. Am. Chem. Soc.*, **95,** 5595 (1973)
(23) L. Ernst, V. Wray, V. A. Chertkov, and N. M. Sergeyev, *J. Magn, Reson.*, **25,** 123 (1977).
(24) S. Gronowitz, I. Johnson, and A. B. Hornfeldt, *Chem. Scr.*, **8,** 8 (1975), and references therein.
(25) M. P. Simonnin, M. J. Pouet, J. M. Cense, and C. Paulmier, *Org. Magn. Reson.* **8,** 508 (1976).
(26) C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90,** 4328 (1968).
(27) S. G. Williams and F. E. Norrington, *J. Am. Chem. Soc.*, **98,** 509 (1976).
(28) W. B. Smith and T. W. Proulx, *Org. Magn. Reson.*, **8,** 567 (1976).
(29) F. Hruska, H. M. Hutton, and T. Schaeffer, *Can. J. Chem.*, **43,** 2392 (1965).
(30) H. Wennerström and O. Wennerström, *Acta Chem. Scand.*, **26,** 2883 (1972).
(31) H. Hosoya, S. Hosoya, and S. Nagakura, *Theor. Chim. Acta*, **12,** 117 (1968).
(32) J. W. Larsen and P. A. Bouis, *J. Am. Chem. Soc.*, **97,** 4418 (1975).
(33) O. A. Gansow and W. Schittenhelm, *J. Am. Chem. Soc.*, **93,** 4294 (1971).