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o-Fluoranil Chemistry: Diels–Alder versus Hetero-Diels–Alder Cycloaddition

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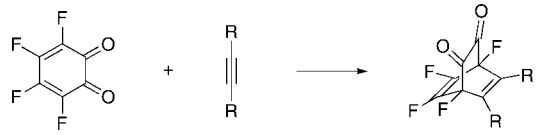
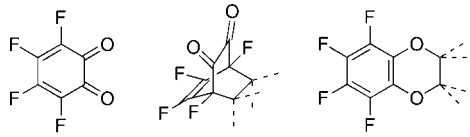


The title quinone undergoes [4 + 2] cycloadditions in two ways, Diels–Alder on the ring and hetero-Diels–Alder by attack at the oxygens. The latter mode of reaction is strongly favored thermodynamically, but there is a kinetic bias favoring the normal Diels–Alder addition that often prevails, especially with cycloaddends that are not electron-rich.

Introduction

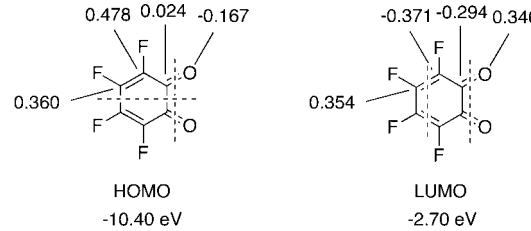
Aside from a brief description of its electrochemistry,[1] the literature contains only a single paper on the chemistry of the title compound, *o*-fluoranil (tetrafluoro-*o*-benzoquinone, **1**). This 1967 report by Shteingarts et al.[2] showed that the quinone can undergo [4 + 2] cycloaddition either by Diels–Alder reaction on the ring diene to give an α-diketone (**2**) or by hetero-Diels–Alder addition on the carbonyl oxygens to give a dioxene (**3**) (or dioxin). *o*-Fluoranil is potentially useful as a $(CF)_4$ synthon, because we have found that normal Diels–Alder reaction followed by 2-fold photodecarbonylation of the α-diketone adduct incorporates a [−CF═CF−CF═CF−] fragment into a molecule.[3] However, it was guesswork as to which of the modes of cycloaddition would occur with a given substrate. The main objective of the present study was to shed light on that issue.



1 **2** **3**

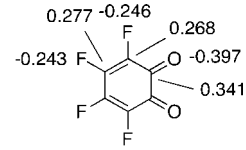
Results and Discussion

Competing Pathways. The quinone's frontier orbitals (AM1)[4] are depicted below. Expected to be the key orbital for



interaction with most substrates, the very low-lying LUMO offers little basis for choice between the two reaction pathways. The HOMO would favor normal Diels–Alder addition, and should be important with electron-deficient substrates.

Atomic charges calculated at the B3LYP/6-31G* level of theory[5] appear below. If charge distribution were the only factor



involved, electron-rich cycloaddends would undergo Diels–Alder reaction preferentially, and electron-poor ones react at the oxygens.

Thermodynamics provides a strong bias toward the latter mode of reaction, mostly because it generates an aromatic ring. For a variety of cycloaddends, Table 1 presents calculated energy changes for both reaction types, together with the product found experimentally. The $\Delta\Delta E$ column shows the invariably

(1) Stallings, M. D.; Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 2655.

(2) Shteingarts, V. D.; Budnik, A. G. *Izv. Sibi. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1967**, 124.

(3) Bogachev, A. A.; Kobrina, L. S. *Russ. J. Org. Chem.* **1997**, *33*, 681–3.

(4) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

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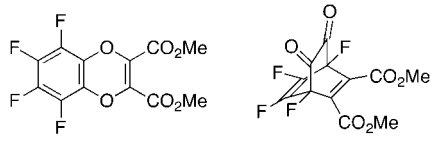
TABLE 1. Calculated Reaction Energies[a] for *o*-Fluoranil and Observed Products

cycloaddend	ΔE_{DA}	$\Delta E_{Diox.}$	$\Delta\Delta E$	product
furan	−7.20[b]	−22.18	−15.0	dioxene
1,4-diphenylbutadiene[c]	−9.59[d]	−26.91	−17.3	dioxene[2]
diphenylketene	−10.68	−43.85	−33.2	dioxene[2]
cyclohexene	−21.25[b]	−35.56	−14.3	dioxene
norbornene	−30.59[e]	−42.07[f]	−11.5	DA adduct
styrene	−20.02[f]	−36.78	−16.8	DA adduct[2]
α-methylstyrene	−21.63[g]	−40.43	−18.8	DA adduct[2]
indene	−22.58[f]	−33.86	−11.3	DA adduct[2]
methyl acrylate	−22.46[b]	−32.94	−10.5	DA adduct
3-hexyne	−36.43	−51.85	−15.4	DA adduct
phenylacetylene	−37.00	−53.06	−16.1	DA adduct[2]
DMAD[h]	−28.74	−52.04	−23.3	DA adduct

[a] In kcal/mol, calculated at the B3LYP/6-31G* level of theory (0 K, without zeropoint energy corrections). [b] Endo. [c] Trans, trans. [d] Styryl exo, phenyl endo. [e] Exo, exo. [f] Exo. [g] Phenyl exo. [h] Dimethyl acetylenedicarboxylate.

large energetic advantage of the hetero-Diels–Alder reaction. Distinction between the two types of adduct is easily made with ^{19}F NMR. The dioxenes display two multiplets in the δ –165 to –170 region for the four fluorines, but the Diels–Alder adducts give rise to peaks in the –150 ppm region for the vinyl fluorines and the −200 ppm region for the bridgehead fluorines. The table makes it clear that charge distribution in the quinone has little influence on the course of the reaction, as some of the most electron-rich cycloaddends (e.g., furan) attack at oxygen, and most electron-deficient ones undergo Diels–Alder reaction.

It is remarkable that Diels–Alder reaction takes place so frequently in the face of unfavorable thermodynamics, most notably in the case of dimethyl acetylenedicarboxylate, where the dioxin (**4**) is >20 kcal/mol more stable than the Diels–Alder adduct (**5**).



4 **5**

The strong kinetic bias toward Diels–Alder reaction is also apparent in the case of phenylacetylene, and Figure 1 shows calculated enthalpy changes in both its Diels–Alder reaction and the unobserved dioxin formation. The two transition states, shown in Figure 2, are quite unsymmetrical, but the net transfer of charge from the acetylene to the quinone is only 0.13 and 0.31 units in the Diels–Alder and dioxin transition states, respectively.

The fact that the reaction is strongly exothermic means that the transition state comes early and is thus less influenced than otherwise by the enthalpy difference between the two possible

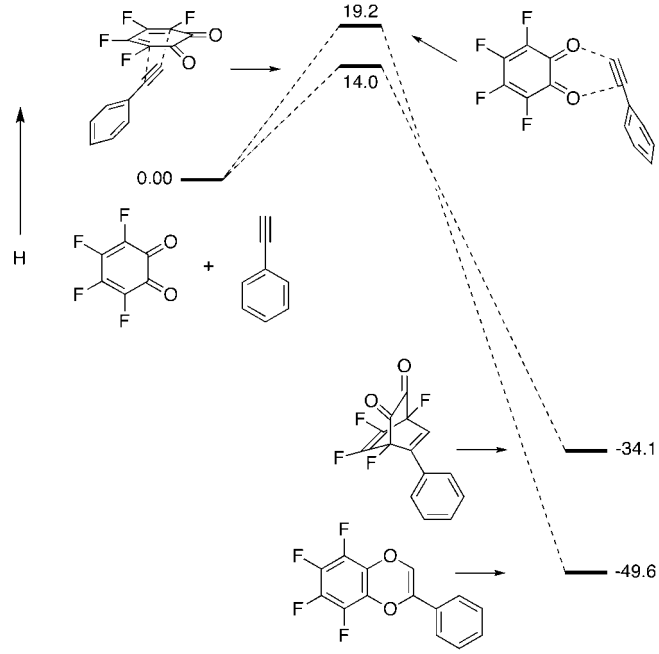


FIGURE 1. Reaction profiles for phenylacetylene/*o*-fluoranil cycloadditions, calculated at the B3LYP/6-31G* level of theory. Enthalpy changes are given in kcal/mol. The entropies of activation and of reaction are large and negative, but very similar for the two reaction types.

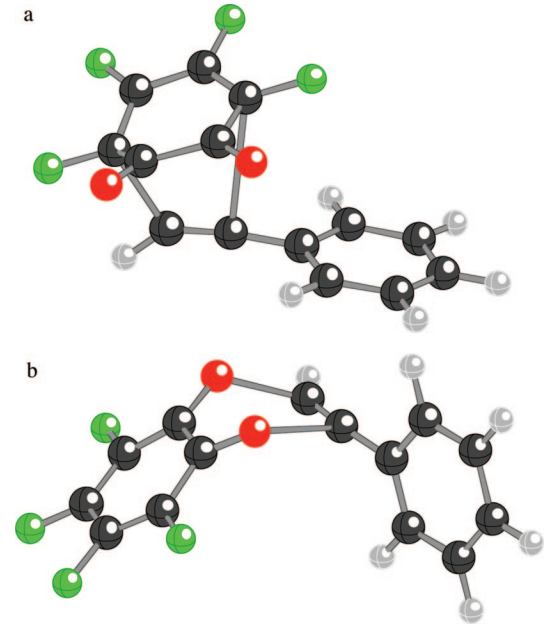


FIGURE 2. Transition states for reactions of phenylacetylene with *o*-fluoranil: Diels–Alder addition (a) and dioxin formation (b), calculated at the B3LYP/6-31G* level of theory.

products.[6] However, the question remains as to the origin of the kinetic bias favoring Diels–Alder reaction. The following three factors probably all contribute to that bias. The increase in transition state energy arising from filled orbital repulsion should be greater for attack at the electron-rich oxygens of the quinone than at the electron-deficient carbons. Rehybridization at carbon of the C−F bonds from sp^2 toward sp^3 should help to

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; and Pople, J. A. *Gaussian 98*, Revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(6) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

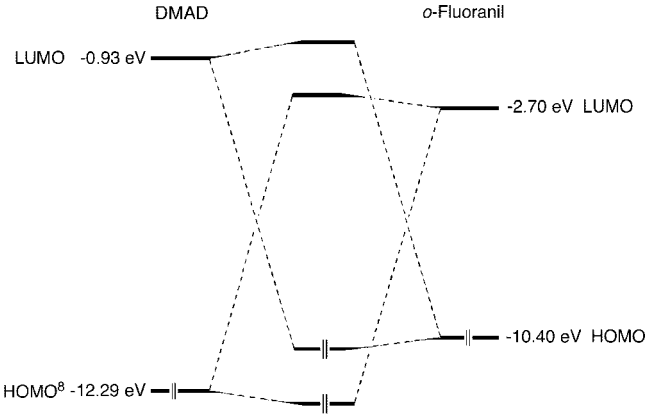


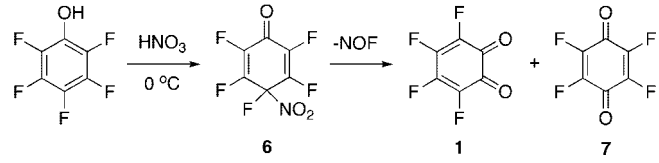
FIGURE 3. Frontier orbital interactions (AM1) in the dimethyl acetylenedicarboxylate/*o*-fluoranil Diels–Alder reaction. HOMO stabilization is 0.022 $(\beta')^2$ for *o*-fluoranil and 0.020 $(\beta')^2$ for DMAD.

stabilize a Diels–Alder transition state (Bent's rule[7]), and finally the much larger coefficient at carbon than at oxygen in the quinone HOMO favors that mode of reaction. The HOMO presumably plays an especially important role in determining the reaction course for the electron-poor substrates methyl acrylate and dimethyl acetylenedicarboxylate, which might not have been expected to react at all with the electron-deficient quinone. For DMAD, the quinone HOMO−acetylene LUMO interaction is as large as the acetylene HOMO−quinone LUMO interaction, as illustrated in Figure 3.

Regarding other entries in Table 1, formation of a dioxene from diphenylketene may be a consequence of the huge difference in reaction energies for the competing pathways, together with steric hindrance to Diels–Alder reaction from the twisted phenyls. One might have anticipated that cyclohexene and norbornene (just a bridged cyclohexene) would react similarly with *o*-fluoranil, but instead they present a sharp contrast. Both react at room temperature, but whereas norbornene yields a pair of stereoisomeric Diels–Alder adducts, cyclohexene gives none. In a messy reaction, it affords the dioxene in roughly 5% yield, and also undergoes slow oxidation to benzene with comcomitant formation of tetrafluorocatechol.[9] Most of the aryl-substituted alkenes in Table 1 yield Diels–Alder adducts, but *trans*,*trans*-1,4-diphenylbutadiene gives a dioxene. Thus, the behavior of alkenes is not completely predictable, but alkynes with substituents ranging from alkyl to methoxycarbonyl afford Diels–Alder adducts. Smaller steric demand in the case of alkynes may be responsible at least in part for the difference.

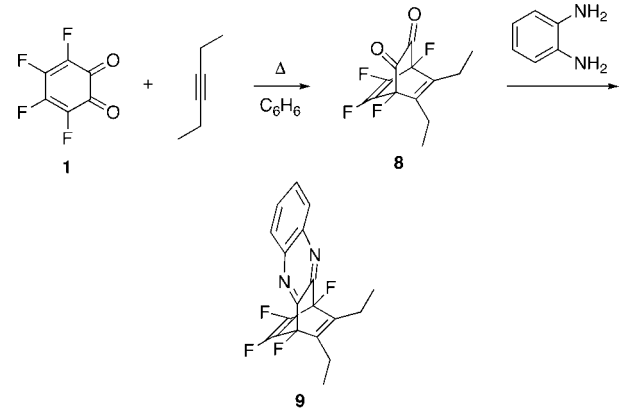
Synthetic Considerations. *o*-Fluoranil has been prepared by nitric acid oxidation of tetrafluorocatechol.[2] The catechol was originally synthesized from hexafluorobenzene in three steps,[10,11] and recently from pentafluorophenol in better yield, again in three steps.[12]

We have made further improvements in the rather labor-intensive synthesis of the quinone, to be published elsewhere. Shteingarts found that oxidaton of pentafluorophenol with nitric



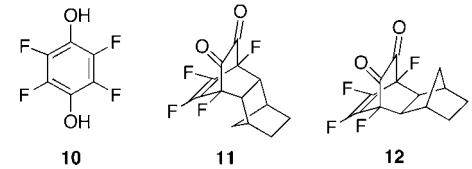
acid gave quinonitrole **6**, which decomposed spontaneously to an inseparable mixture of *o*- and *p*-fluoranil (**7**).[13] Because the ortho isomer is far more reactive than the para, it is often practical to use this easily prepared mixture for reactions of the *o*-quinone, with its isomer **7** remaining unchanged for separation in the workup. The quinone mixture was used exclusively in the present work.

When the reaction product is a dioxene, quinone **7** can be removed by extraction with sodium bisulfite solution. As electron-deficient α-diketones, Diels–Alder adducts of *o*-fluoranil react with water voraciously, and the Russian workers isolated them by taking advantage of the insolubility in benzene of their highly polar hydrates.[2] In the present work, we have derivatized the Diels–Alder adducts with *o*-phenylenediamine, forming qui-



noxalines such as **9** from dione **8**.[14] *p*-Fluoranil is reduced by the diamine to tetrafluorohydroquinone (**10**), identified by comparison with an authentic sample, and the diamine forms highly colored oxidation products. Extraction with sodium carbonate solution removes the hydroquinone.

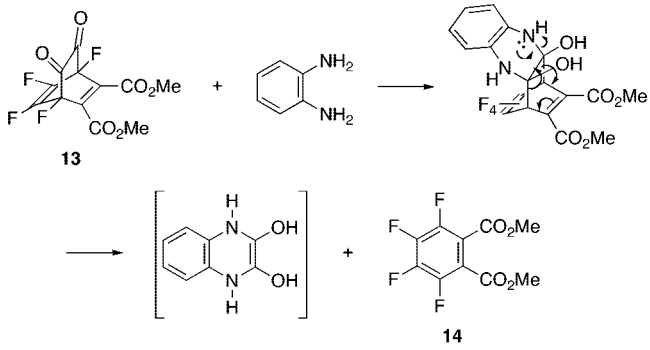
The two diones formed in the ratio 4:1 from the reaction of *o*-fluoranil with norbornene behaved differently toward the diamine. The major isomer reacted readily but the minor one with reluctance, presumably for steric reasons. Their configurations have not been established, but the reactivity difference supports assignment of the major isomer as **11** and the minor one as **12**, endo and exo, respectively, on the new 6-membered ring (both probably exo with respect to the norbornene ring, again for steric reasons).



Surprisingly, the reaction of *o*-phenylenediamine with the Diels–Alder adduct **13** derived from dimethyl acetylenedicarboxylate gave only a small yield of the quinoxaline, the major product being dimethyl tetrafluorophthalate (**14**). Under very mild conditions, the diamine had induced loss of the dicarbonyl bridge, perhaps via the mechanism shown in Scheme 1,

(7) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.
(8) This orbital is actually the HOMO-3, as the slightly higher lying top three occupied orbitals are concentrated on the oxygens.
(9) Both Diels−Alder and hetero-Diels−Alder reaction are much more exothermic with norbornene, so again an earlier transition state helps to explain the contrasting behavior. The product energy difference favoring dioxene is also somewhat smaller in the case of norbornene (Table 1).
(10) Burdon, J.; Damodaran, V. A.; Tatlow, J. C. *J. Chem. Soc.* **1964**, 763.
(11) Macdonald, C.; Tomlinson, A. J.; Willis, C. J. *Can. J. Chem.* **1971**, *49*, 2578.

SCHEME 1



concerted or stepwise. Stabilization of developing negative charge by a methoxycarbonyl group presumably explains why bridge loss occurred here but not when the 3-hexyne and phenylacetylene adducts were treated with *o*-phenylenediamine.

Conclusions

Thermodynamics greatly favors dioxene (or dioxin) formation over Diels–Alder addition in the reactions of *o*-fluoranil with a broad spectrum of cycloaddends. Nonetheless, there exists a strong kinetic preference for the latter mode of reaction that often overcomes the thermodynamic bias, particularly in the case of substrates that are not electron-rich. Alkynes in general undergo Diels–Alder reaction, but prediction about reaction pathways for some other cycloaddends is risky because countervailing factors are closely balanced. The fact that Diels–Alder addition occurs with a variety of substrates bodes well for use of *o*-fluoranil as a $(CF)_4$ synthon.

Experimental Section

Tetrafluorobenzoquinones (1, 7).[14] Pentafluorophenol (6.00 g, 32.6 mmol), melted with a heat gun, was added rapidly dropwise with stirring to concentrated nitric acid (20 mL) that had been cooled in an ice bath. The mixture became yellow and set to a crystalline mass. After several minutes the solid was collected by filtration, washed well with ice–water, and sucked dry. Initially pale yellow, this quinonitrole became yellower as it began to decompose to the quinones, so it was quickly dissolved in 20 mL of CH_2Cl_2 and dried with $MgSO_4$ followed by a little P_4O_{10} to preclude destruction of the sensitive *o*-quinone by water. After filtration, the solution was refluxed for 40–50 min to complete conversion to the quinone mixture. The solution was then decanted or filtered to leave behind a small amount of white solid derived from the extruded nitrosyl fluoride. Evaporation of the solvent left 5.28 g (29.3 mmol, 90% yield) of orange-red crystals. ^{19}F NMR ($CDCl_3$): ortho-isomer δ −135.7 (s, 2F), −150.2 (s, 2F); para-isomer δ −140.0 (s, 4F). No other signals were present in the spectrum, and the ^{1}H NMR spectrum showed no proton-containing impurities. The ortho/para ratio was 61:39, representing a yield of 55% for the *o*-quinone.

***cis*-5,6,7,8-Tetrafluoro-3a,9a-*H*-furo[2,3-*b*][1,4]benzodioxin.** In a 25 mL round-bottomed flask were combined 1.00 g of the quinone mixture (61:39 o/p ratio, 3.39 mmol of *o*-fluoranil), 3 mL of freshly distilled furan (2.8 g, 41 mmol), 10 mL of benzene, and a spatulaful of $CaCO_3$ to scavenge adventitiously formed HF. The mixture, which rapidly darkened, was stirred at rt for 40 h, at which time very little *o*-fluoranil remained. The dark brown mixture was extracted with 10 mL of 10% aqueous $NaHSO_3$ solution to remove the unreacted *p*-quinone, followed by 10 mL of brine. Dried over $MgSO_4$, the organic phase was filtered and evaporated to leave a dark brown syrup. A 0.5 g portion of this syrup was chromatographed on 12.5 g of silica gel with CH_2Cl_2 as eluent, giving 211 mg of orange crystals of the dioxene (37% yield based on total product). Purification by low-temperature recrystallization from hexane followed by sublimation gave white needles, mp 68–69 °C. ^{19}F NMR ($CDCl_3$): δ −162.5 (ddd, J = 21.7, 7.6, 3.1 Hz, C_5 or C_8, 1F), −163.3 (ddd, J = 21.7, 7.6, 3.9 Hz, C_5 or C_8, 1F), −165.8 (td, J = 21.7, 3.1 Hz, C_6 or C_7, 1F), −166.8 (td, J = 21.7, 3.9 Hz, C_6 or C_7, 1F). ^{1}H NMR ($CDCl_3$): δ 6.57 (dd, J = 2.82, 1.41, C_2H), 6.22 (d, J = 6.49, C_{9a}H), 5.64 (ddd, J = 2.82, 1.98, 1.41 Hz, C_{3a}H), 5.15 (dd, unresolved, J =1.98, 1.41 Hz, C_3H). ^{13}C NMR (^{19}F decoupled, $CDCl_3$): δ 151.2 (dm, $^1J_{CH}$ = 196 Hz, vinyl C), 139.5 (aryl CO), 138.55 (CF), 138.52 (CF), 137.5 (CF), 136.7 (CF), 136.5 (aryl CO), 130.3 (dd, $^1J_{CH}$ = 233, 6.4 Hz, vinyl C), 100.4 (ddm, $^1J_{CH}$ = 183, 38 Hz, bridgehead C), 79.4 (dm, $^1J_{CH}$ = 164 Hz, bridgehead C). IR (C_2Cl_4): 2963, 1750, 1616, 1510, 1464, 1357, 1261, 1103, 1046 cm^{-1}. Anal. Calcd for $C_{10}H_4F_4O_3$: C, 48.40; H, 1.62; F, 30.63. Found: C, 48.39; H, 1.61; F, 30.49.

1,4-Dihydro-2,3-diethyl-1,4,11,12-tetrafluoro-1,4-ethenophenazine (9). In a 25 mL round-bottomed flask were placed 2.94 g of quinone mixture (1.78 g of *o*-quinone, 9.89 mmol), 4.0 mL (2.9 g, 35 mmol) of 3-hexyne, and 15 mL of benzene. The mixture, which rapidly became black, was refluxed for 31 h, after which no *o*-quinone remained. ^{19}F NMR ($CDCl_3$): δ –152.9 (vinyl F, 2F), −209.6 (bridgehead F, 2F) for the dione adduct, NMR yield 65%. A solution of 1.08 g (10 mmol) of *o*-phenylenediamine in 5 mL of warm benzene was added and the mixture was boiled for 3 min. The ^{19}F NMR spectrum showed only three significant signals, two for the desired quinoxaline and one for tetrafluorohydroquinone. Evaporation of the solvent left 4.88 g of dark brown residue. A portion (26%) of this product was dissolved insofar as possible in 20 mL of CH_2Cl_2, and extraction with 10 mL of 5% NaOH resulted in copious precipitation of brown solid. The organic layer was separated, washed with 10 mL of water, and dried over $MgSO_4$. Filtration and evaporation of the solvent gave 404 mg of brown solid, which was chromatographed on 12 g of silica gel with 20% ethyl acetate/hexanes as eluent. The resulting quinoxaline (350 mg, 41% crude yield) was sublimed (∼90 °C, 20 mTorr) and finally recrystallized from methanol to afford 230 mg of colorless blocks, mp 155–157.5 °C. ^{1}H NMR ($CDCl_3$): δ 8.09, 7.78 (A_2X_2, aryl H, 4H), 2.45 (m, CH_2, 4H), 1.07 (t, J = 7.7 Hz, CH_3, 6H). ^{19}F NMR ($CDCl_3$): δ –155.0 (s, vinyl F, 2F), –212.6 (s, bridgehead F, 2F). ^{13}C NMR ($CDCl_3$): δ 150.8 ("C═N"); 142.8 (C—CH_2); 141.5 (vinyl C—F, $^1J_{CF}$ = 292 Hz), 137.7 ("C—N"), 130.4, 128.9 (aryl CH), 91.4 (bridgehead CF, $^1J_{CF}$ = 219 Hz), 19.0 (CH_2), 13.4 (CH_3). IR (C_2Cl_4): 2966, 1749, 1508, 1461, 1331, 1290, 1232, 1190, 1061, 950, 855 cm^{-1}. Anal. Calcd for $C_{18}H_{14}F_4N_2$: C, 64.66; H, 4.22; N, 8.38. Found: C, 64.74; H, 4.19; N, 8.41.

Dimethyl 1,4-Dihydro-1,4,11,12-tetrafluoro-1,4-ethenophenazine-2,3-dicarboxylate. In a 25 mL round-bottomed flask were placed 2.01 g of the quinone mixture (1.31 g *o*-quinone, 7.28 mmol), 1.17 g (8.20 mmol) of dimethyl acetylenedicarboxylate, and 5 mL of freshly distilled toluene. Reaction was complete after the dark red solution had been refluxed for 19 h. ^{19}F NMR ($CDCl_3$): δ −148.5 (vinyl f, 2F), −206.2 (bridgehead F, 2F) for the dione adduct. A solution of *o*-phenylenediamine (0.80 g, 7.4 mmol) in 8 mL of warm CH_2Cl_2 was added portionwise by pipet to the cooled reaction mixture. After filtration to remove 1.5 g of insoluble material and evaporation of the solvent, the resulting brown tar (2.65 g) was redissolved in 35 mL of CH_2Cl_2 and extracted with 20 mL of 5% Na_2CO_3 solution. A second extraction with 10 mL of 10% Na_2CO_3 followed to ensure complete removal of the tetrafluorohydroquinone. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was chromatographed on silica gel (24 g) with 20% ethyl acetate/hexanes as eluent. Early fractions yielded dimethyl tetrafluorophthalate (836 mg, 43% crude yield),

(12) Barthel, J.; Bustrich, R. German patent DE 19633027, 1988.
(13) Shteingarts, V. D.; Budnik, A. G.; Yakobson, G. G.; Vorozhtsov, N. N., Jr. *Zh. Obsch. Khim.* **1967**, *37*, 1537.
(14) The Russian group also prepared quinoxalines from their hydrates (ref 2).

and later ones the quinoxaline (153 mg, 5.3% crude yield). Recrystallizations from hexanes with charcoal treatment gave pure phthalate as fine, white crystals, mp 72–73.5 °C (lit.[15] 73–73.5 °C). ^{1}H NMR ($CDCl_3$): δ 3.94. ^{19}F NMR ($CDCl_3$): δ −137.0, −149.2. Recrystallizations of the quinoxaline from methanol with charcoal treatment yielded white crystals melting at 190–191 °C. ^{19}F NMR ($CDCl_3$): δ −151.1 (s, vinyl F, 2F), −209.8 (s, bridgehead F, 2F). ^{1}H NMR ($CDCl_3$): δ 8.16 (m, aryl H, 2H), 7.84 (m, aryl H, 2H), 2.91 (m, CH_3, 6H). ^{13}C NMR ($CDCl_3$): δ 160.3 (C═O), 148.3 ("C═N"), 143.6 (C—CO), 141.6 (vinyl CF, $^1J_{CF}$ = 295 Hz), 138.0 ("C—N"), 131.5, 129.3 (aryl CH), 90.0 (bridgehead CF, $^1J_{CF}$ = 228 Hz), 53.5 (CH_3). IR (C_2Cl_4): 2960, 1750, 1718, 1700, 1514, 1433, 1318, 1263, 842 cm^{-1}. Anal. Calcd for $C_{18}H_{10}F_4N_2O_4$: C, 54.83; H, 2.56; N, 7.11. Found: C, 55.00; H, 2.50; N, 6.99.

Methyl 1,4-Dihydro-1,2,3,4-tetrafluoro-1,4-ethanophenazine-11-carboxylate. In a 25 mL round-bottomed flask were placed a quinone mixture (1.23 g of ortho-isomer, 6.84 mmol), benzene (10 mL), and 1.0 mL (0.96 g, 11 mmol) of methyl acrylate. Reaction was complete after the resulting solution was refluxed for 18 h. The ^{19}F NMR spectrum ($CDCl_3$), showed signals for the Diels–Alder adduct at δ −144.6, −147.4 (vinyl Fs) and –193.8, –194.8 (bridgeheads Fs). *o*-Phenylenediamine (0.8 g, 7 mmol) was added in 6 mL of benzene, and the orange solution instantly became black. After 5 min at reflux, the mixture was evaporated to a dark brown tar. A sample of the tar (1.495 g, 45.0% of the total) was chromatographed on 20 g of silica gel with 20% ethyl acetate/hexanes as eluent, giving 686 mg of crude quinoxaline (66% yield). Recrystallization from methanol followed by sublimation at 100 °C and 30 mTorr gave analytically pure, microcrystalline product, mp 167.5–168 °C. Its stereochemistry has not been determined. ^{19}F NMR ($CDCl_3$): δ −149.4 (s, vinyl F, 1F), −152.6 (s, vinyl F, 1F), −198.8 (s, bridgehead F, 1F), −200.1 (s, bridgehead F, 1F). ^{1}H NMR ($CDCl_3$): δ 8.21 (m, aryl, 2H), 7.88 (m, aryl, 2H), 3.89 (s, methyl, 3H), 3.31 (m, 3° H, 1H), 2.76 (m, methylene, 1H), 2.62 (m, methylene, 1H). ^{13}C NMR ($CDCl_3$): δ 169.8 (C═O), 148.7, 148.6 ("C═N"), 140.1 ("C—N"), 137.0 (vinyl CF, $^1J_{CF}$ = 287 Hz), 135.3 (vinyl CF, $^1J_{CF}$ = 290 Hz), 131.1, 129.4 (aryl CH), 89.9 (bridgehead CF, $^1J_{CF} \approx$ 218 Hz), 88.2 (bridgehead CF, $^1J_{CF} \approx$ 218 Hz), 52.7 (CH_3), 44.1 (CH), 35.9 (CH_2). IR (C_2Cl_4): 3033, 2956, 1739, 1506, 1439, 1350, 1272, 1244, 1211, 1172, 1094, 1033, 956 cm^{-1}. Anal. Calcd for $C_{16}H_{10}F_4N_2O_2$: C, 56.81; H, 2.98; N, 8.28. Found: C, 56.81; H, 2.93; N, 8.29.

(15) Yakobson, G. G.; Odinokov, V. N.; Yorozhtsov, N. N., Jr. *Zh. Obsch. Khim.* **1966**, *36*, 139.

6,6a,7,8,9,10,10a,11-Octahydro-6,11,13,14-tetrafluoro-6,11-etheno-7,10-methanobenzo[*b*]phenazine. A quinone mixture (266 mg of ortho-isomer, 1.48 mmol), norbornene (190 mg, 2.02 mmol), and CH_2Cl_2 (4 mL) were combined in a 10 mL round-bottom flask, and the solution was refluxed. Complete after a few hours, the reaction gave two Diels–Alder adducts in a ratio of ca. 4:1. The ^{19}F NMR spectrum ($CDCl_3$) showed signals at δ –146.2 (vinyl Fs), –195.6 (bridgehead Fs) for the major adduct, and at –147.9 (vinyl Fs), –194.7 (bridgehead Fs) for the minor one. *o*-Phenylenediamine (168 mg, 1.56 mmol) was added, and the resulting black mixture was refluxed for 20 min. The major adduct was converted completely to its quinoxaline derivative, but much of the minor one survived. After evaporation of the solvent, the dark residue was heated and triturated with $CHCl_3$, but some black polymeric material remained undissolved. The slurry was placed on a column of silica gel (12 g), and elution followed with 20% ethyl acetate/hexanes. Successive fractions of 238 mg (major quinoxaline) and 59 mg (ca. 2:1 major/minor quinoxaline) were obtained (58% total yield). ^{19}F NMR ($CDCl_3$) for the minor isomer: δ –147.9 (s, vinyl F, 2F), −194.7 (s, bridgehead F, 2F). The first fraction was recrystallized from hexanes, then from methanol to give the major isomer as colorless needles, mp 181–181.5 °C. ^{19}F NMR ($CDCl_3$): δ −151.3 (s, vinyl F, 2F), −201.68 (s, bridgehead F, 2F). ^{1}H NMR ($CDCl_3$): δ 8.25 (m, aryl H, 2H), 7.83 (m, aryl H, 2H), 2.85 (s, bridgehead H proximal to F, 2H), 2.33 (s, distal bridgehead H, 2H), 2.10 (d, J = 11.7 Hz, one-C bridge H, 1H), 1.70 (m, two-C bridge H, 2H), 1.26 (d, J = 11.7 Hz, one-C bridge H, 1H), 1.19 (m, two-C bridge H, 2H). ^{13}C NMR ($CDCl_3$): δ 149.4 ("C═N"), 139.0 ("C—N"), 134.1 (vinyl CF, $^1J_{CF}$ = 288 Hz), 130.7, 129.4 (aryl CH), 90.5 (bridgehead CF, $^1J_{CF}$ = 217 Hz), 51.1 (bridgehead CH, proximal to F), 37.2, 33.7, 30.1 (CH, CH_2). IR (C_2Cl_4): 2968, 1740, 1504, 1359, 1323, 1220, 1184, 1093, 1039, 997, 954 cm^{-1}. Anal. Calcd for $C_{19}H_{14}F_4N_2$: C, 65.89; H, 4.07; N, 8.09. Found: C, 65.88; H, 4.06; N, 8.09. in.

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Supporting Information Available: Total energies at the B3LYP/6-31G* level of theory, general experimental information, and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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