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The Elusive Antiaromaticity of Maleimides and Maleic Anhydride: Enthalpies of Formation of *N*-Methylmaleimide, *N*-Methylsuccinimide, *N*-Methylphthalimide, and *N*-Benzoyl-*N*-methylbenzamide

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In order to understand the antiaromaticity of maleimides, the enthalpies of formation and sublimation of *N*-methylmaleimide, *N*-methylsuccinimide, *N*-methylphthalimide, and *N*-benzoyl-*N*-methylbenzamide were measured. The numerical values of enthalpies of formation for these compounds in the solid state are −329.3 ± 1.4, −469.8 ± 1.6, −325.0 ± 2.1, and −239.6 ± 3.8 kJ mol^{-1}, respectively, while the corresponding values in the gaseous state are −256.0 ± 1.5, −389.7 ± 1.6, −233.9 ± 2.2, and −119.5 ± 3.8 kJ mol^{-1}, respectively. The values of enthalpies of sublimation for the same compounds are 73.3 ± 0.5, 80.1 ± 0.3, 91.1 ± 0.5, and 120.1 ± 0.4 kJ mol^{-1}, respectively. We find that the antiaromaticity of maleimides is only modest.

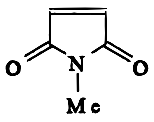
Introduction

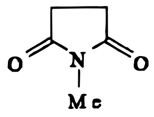
The variously *N*-substituted maleimides and maleic anhydride are well established to be highly reactive dienophiles in the Diels−Alder reaction.[1] Their ring opening[2] and addition across the carbon−carbon double bond[3] are well-known to be highly facile. These phenomena have been interpreted as manifestations of antiaromaticity[4,5] arising from the formal presence of 4π ring electrons.[6] The current study discusses this antiaromaticity in terms of measured (condensed and gas phase) enthalpies of formation of *N*-methylmaleimide, maleic anhydride, and some related species.[7]

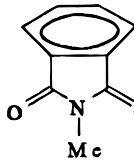
Since we wish to consider the intrinsic destabilization of the maleimides and maleic anhydride, implicitly all thermochemical quantities below will refer to species in their gas phase under the standard conditions of 25 °C and 1 atm (or more "properly" 298.15 K and 101.325 kPa, respectively). We will discuss various precedented approaches to aromaticity in various carbocycles and heterocycles and see what they indicate about the degree of antiaromaticity in maleimides and maleic anhydride.

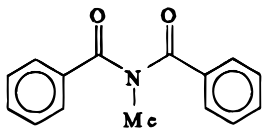
Results

The results of the combustion experiments carried out with *N*-methylmaleimide, *N*-methylsuccinimide, *N*-methylphthalimide, and *N*-benzoyl-*N*-methylbenzamide are given in Table 1. The symbols in this table have the same meaning, and the experimental values have been derived as in ref 8a. The specific energy of combustion of the four compounds are referred to the final temperature of the experiments, 298.15 K. Table 2 gives the standard molar energy and enthalpy of combustion and the standard molar enthalpy of formation of *N*-methylmaleimide, *N*-methylsuccinimide, *N*-methylphthalimide, and *N*-benzoyl-*N*-methylbenzamide in the crystalline state at T = 298.15 K.









The uncertainties of the standard molar energy and enthalpy of combustion are twice the final overall standard deviation of the mean and were estimated as outlined by Olofsson.[8b] The values for the standard molar enthalpies of formation of H_2O(l) and CO_2(g) at T =

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(5) Tobia, D.; Harrison, R.; White, T. L.; DiMare, M.; Rickborn, B. *J. Org. Chem.* **1993**, *58*, 6701.

(6) This assignment arises from counting the π electrons as two from the carbon−carbon double bond and two from the nitrogen or oxygen as is done to arrive at an aromatic count to six electrons in pyrrole or furan, respectively. The two carbonyl groups are considered not to contribute electrons at all as done to arrive at six electrons for either 2- or 4-pyridone to be considered aromatic.

(7) We accept the value of the enthalpy of formation of maleic anhydride from the literature, as well as that of many ancillary substances. Unless otherwise said, these and any other unreferenced data will be taken from the following archive: Pedley, J. B. *Thermochemical Data of Organic Compounds*, 3rd ed.; Thermochemical Research Center: College Station, TX, 1994.

(8) (a) Westrum, E. F., Jr. Presentation of combustion calorimetric data in the primary literature. In *Combustion Calorimetry*; Sunner, S., Mänsson, M., Eds.; Pergamon Press: Oxford, 1979; Chapter 7. (b) Olofsson, G. Assignment of uncertainties. In *Combustion Calorimetry*; Sunner, S., Mänsson, M., Eds.; Pergamon Press: Oxford, 1979; Chapter 6. (c) CODATA. Recommended key values for thermodynamics, 1975. *J. Chem. Thermodyn.* **1976**, *8*, 603.

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Table 1. Results of Combustion Experiments ($p^0 = 101.325$ kPa)[a]

N-Methylmaleimide

m' (compound)^b/g	0.63722	0.63949	0.64340	0.63686	0.63477
m'' (polyethylene)^b/g	0.04982	0.05365	0.05412	0.05590	0.05430
$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{corr})/\mathrm{K}$	1.1111	1.1282	1.1353	1.1313	1.1230
ϵ(calor)^c $(-\Delta t_c)$/kJ	−15.8758	−16.1201	−16.2218	−16.1645	−16.0463
ϵ(cont)^d $(-\Delta t_c)$/kJ	−0.0181	−0.0184	−0.0185	−0.0185	−0.0183
$\Delta U_{ign}{}^e$/kJ	0.0414	0.0472	0.0484	0.0439	0.0474
ΔU_{dec} (HNO$_3$)^f/kJ	0.0414	0.0414	0.0414	0.0443	0.0420
ΔU(corr to std states)^g/kJ	0.0110	0.0111	0.0112	0.0111	0.0110
$-m''\Delta_c u^\circ$(polyethylene)/kJ	2.3102	2.4879	2.5098	2.5924	2.5178
$\Delta_c u^\circ$(compound)/(kJ g^{-1})	−21.1699	−21.1902	−21.1836	−21.1841	−21.1831
$<\Delta_c u^\circ(298.15\ \mathrm{K})>$/(kJ g^{-1})	−21.1822 ± 0.0033				

N-Methylsuccinimide

m' (compound)^b/g	0.62097	0.62307	0.62382	0.59409	0.60463	0.60310	0.59845
m'' (polyethylene)^b/g	0.05491	0.05894	0.04289	0.04819	0.04971	0.04626	0.05075
$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{corr})/\mathrm{K}$	1.1418	1.1587	1.1086	1.0785	1.1011	1.0871	1.0936
ϵ(calor)^c $(-\Delta t_c)$/kJ	−16.3276	−16.5699	−15.8551	−15.4237	−15.7476	−15.5472	−15.6400
ϵ(cont)^d $(-\Delta t_c)$/kJ	−0.0186	−0.0189	−0.0180	−0.0175	−0.0179	−0.0176	−0.0177
$\Delta U_{ign}{}^e$/kJ	0.0469	0.0493	0.0465	0.0477	0.0471	0.0471	0.0480
ΔU_{dec}(HNO$_3$)^f/kJ	0.0406	0.0424	0.0429	0.0406	0.0428	0.0414	0.0414
ΔU(corr to std states)^g/kJ	0.0097	0.0098	0.0096	0.0092	0.0093	0.0093	0.0093
$-m''\Delta_c u^\circ$(polyethylene)/kJ	2.5462	2.7329	1.9890	2.2346	2.3051	2.1449	2.3534
$\Delta_c u^\circ$(compound)/(kJ g^{-1})	−22.0668	−22.0752	−22.0979	−22.0658	−22.0981	−22.0894	−22.0663
$<\Delta_c u^\circ(298.15\ \mathrm{K})>$/(kJ g^{-1})	−22.0799 ± 0.0056						

N-Methylphthalimide

m' (compound)^b/g	0.61278	0.61039	0.61031	0.61017
$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{corr})/\mathrm{K}$	1.1270	1.1230	1.1227	1.1222
ϵ(calor)^c $(-\Delta t_c)$/kJ	−16.1029	−16.0453	−16.0411	−16.0347
ϵ(cont)^d $(-\Delta t_c)$/kJ	−0.0181	−0.0180	−0.0180	−0.0180
$\Delta U_{ign}{}^e$/kJ	0.0473	0.0468	0.0450	0.0467
ΔU_{dec}(HNO$_3$)^f/kJ	0.0325	0.0331	0.0337	0.0325
ΔU(corr to std states)^g/kJ	0.0116	0.0115	0.0115	0.0115
$\Delta_c u^\circ$(compound)/(kJ g^{-1})	−26.1588	−26.1667	−26.1652	−26.1599
$<\Delta_c u^\circ(298.15\ \mathrm{K})>$/(kJ g^{-1})	−26.1627 ± 0.0019			

N-Benzoyl-*N*-methylbenzamide

m' (compound)^b/g	0.53870	0.50709	0.49262	0.49271	0.49215
m'' (polyethylene)^b/g	0.06103	0.04825	0.04665	0.05449	0.04715
$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{corr})/\mathrm{K}$	1.3848	1.2742	1.2369	1.2629	1.2381
ϵ(calor)^c $(-\Delta t_c)$/kJ	−19.8111	−18.2299	−17.6963	−18.0677	−17.7125
ϵ(cont)^d $(-\Delta t_c)$/kJ	−0.0226	−0.0206	−0.0199	−0.0204	−0.0200
$\Delta U_{ign}{}^e$/kJ	0.0474	0.0455	0.0480	0.0442	0.0469
ΔU_{dec}(HNO$_3$)^f/kJ	0.0284	0.0248	0.0236	0.0254	0.0254
ΔU(corr to std states)^g/kJ	0.0111	0.0103	0.0100	0.0101	0.0100
$-m''\Delta_c u^\circ$(polyethylene)/kJ	2.8302	2.2375	2.1634	2.5268	2.1866
$\Delta_c u^\circ$(compound)/(kJ g^{-1})	−31.4026	−31.4193	−31.4060	−31.4213	−31.4207
$<\Delta_c u^\circ(298.15\ \mathrm{K})>$/(kJ g^{-1})	−31.4140 ± 0.0040				

[a] For the definition of the symbols, see refs 4, 7. $T_{th} = 298.15$ K; $V_{bomb} = 0.380$ l. [b] Corrected masses obtained from weight by calculating the buoyancy. [c] ϵ(calor) is the energy equivalent of the whole system minus the content of the bomb. [d] ϵ(cont) energy equivalent of the contents of the bomb $\epsilon(\mathrm{cont})(-\Delta T_c) = \epsilon^i_{con}(T^i - 298.15\ \mathrm{K}) + \epsilon^f_{con}(298.15\ \mathrm{K} - T^f + \Delta T_{corr})$. [e] Experimental energy of ignition. [f] Experimental energy of formation of HNO$_3$. [g] ΔU(corr to std states) is the sum of items 81−85, 87−90, 95, and 94 in ref 25.

Table 2. Standard Molar Energies of Combustion and Enthalpies of Combustion and Formation at Temperature $T = 298.15$ K

compound	$\Delta_c U^\circ{}_m$/ (kJ mol^{-1})	$\Delta_c H^\circ{}_m$/ (kJ mol^{-1})	$\Delta_f H^\circ{}_m$/ (kJ mol^{-1})
N-methylmaleimide	−2353.4 ± 1.3	−2352.8 ± 1.3	−329.3 ± 1.4
N-methylsuccinimide	−2497.5 ± 1.5	−2498.1 ± 1.5	−469.8 ± 1.6
N-methylphthalimide	−4216.4 ± 1.8	−4217.0 ± 1.8	−325.0 ± 2.1
N-benzoyl-*N*-methylbenzamide	−7516.5 ± 3.2	−7520.9 ± 3.2	−239.6 ± 3.8

298.15 K: −(285.830 ± 0.042) and −(393.51 ± 0.13) kJ mol^{-1}, respectively, were taken from CODATA.[8c]

The results of our Knudsen effusion experiments are summarized in Table 3; temperature is reported in K, time in seconds, and mass of sublimed substance in milligrams.

The vapor pressures were calculated by means of the equation

$$p = (\Delta m/W_a a t)(2\pi RT/M)^{1/2} \qquad (1)$$

where p represents the vapor pressure, Δm is the mass loss during the time t, W_a is the Clausing coefficient of the Knudsen cell orifice, a is the area of the effusion orifice, R is the gas constant, T is the temperature, and M is the molar mass of the studied compound.

An equation of the type

$$\lg(p/Pa) = -B(T/K)^{-1} + A \qquad (2)$$

was fitted to the results of Table 4 by the least-squares method. The quantities $\delta p/p$ are the fractional deviations of the experimental vapor pressures from those computed using eq 2. The highest percentage error for the vapor pressure in Table 3 is 0.5, arising from all quantities in eq 1. The parameters A and B of the equations corresponding to *N*-methylmaleimide, *N*-methylsuccinimide, *N*-methylphthalimide, and *N*-benzoyl-*N*-methylbenzamide are given in Table 4. The enthalpies of sublimation, corresponding to the mean temperature θ of their experimental ranges, have been calculated from the corresponding B values and are also collected in Table 4. The uncertainties assigned to the values of $\Delta_{sub}H^\circ{}_m$ are based on the standard deviations of B values.

Table 3. Vapor Pressures

T^a/K	t^b/s	Δm^c/mg	p^d/Pa	$10^2\delta p^e/p$	T^a/K	t^b/s	Δm^c/mg	p^d/Pa	$10^2\delta p^e/p$
N-Methylmaleimide									
276.15	15780	4.71	1.41	−0.3	282.87	11760	7.58	3.07	−0.5
278.24	15360	5.89	1.81	−0.01	286.01	11880	10.71	4.32	−1
280.30	10320	4.98	2.29	−0.4	289.07	12840	16.32	6.13	−0.03
N-Methylsuccinimide									
280.17	15780	3.95	0.265	0.9	291.89	14160	13.86	1.06	0.7
282.98	13380	4.65	0.37	−0.09	294.85	14400	19.40	1.46	−0.7
285.96	12600	6.23	0.53	−0.2	297.95	15780	30.05	2.08	0.5
288.97	10800	7.51	0.75	−0.8					
N-Methylphthalimide									
298.30	16140	0.91	0.0513	1	310.42	23820	5.37	0.21	−0.7
301.38	21780	1.73	0.0730	−0.7	313.30	27300	8.50	0.29	−0.2
303.22	20940	2.09	0.0919	0.3	316.26	16320	7.13	0.41	1
307.26	22620	3.57	0.147	−0.2					
N-Benzoyl-*N*-methylbenzamide									
345.57	12960	4.26	0.266	0.7	357.80	35780	15.87	1.06	0.1
348.74	19440	9.15	0.382	−0.07	359.82	10140	16.18	1.32	−0.09
351.84	21300	14.16	0.542	−0.6	363.67	11400	27.56	2.00	0.1
352.67	20820	15.32	0.600	0.2	366.88	14640	49.78	2.83	1
354.70	23640	21.44	0.742	−1					

[a] Temperature in K. [b] Time length of the experiment in seconds. [c] Mass of sublimed substance in mg. [d] Vapor pressure in Pa. [e] Fractional deviations of the experimental vapor pressures from the values computed using eq 2.

Table 4. Molar Enthalpies of Sublimation

compound	θ/K	A	B	$\Delta_{\text{sub}}H^\circ_{\text{m}}(\theta)$/(kJ mol^{-1})
N-methylmaleimide	282.61	14.4 ± 0.1	3935 ± 26	75.3 ± 0.5
N-methylsuccinimide	289.06	14.4 ± 0.1	4208 ± 17	80.6 ± 0.3
N-methylphthalimide	307.28	14.6 ± 0.1	4750 ± 26	91.1 ± 0.5
N-benzoyl-*N*-methylbenzamide	356.23	17.1 ± 0.1	6070 ± 21	116.8 ± 0.4

The enthalpy of sublimation at $T = 298.15$ K has been computed using the same equation as in ref 27b. The $C^0_{\text{p,m}}$(cr) values have been determined by DSC, and $C^0_{\text{p,m}}$(g) values were calculated using the group-contribution scheme of Rihani and Doraiswamy.[9]

The experimental molar heat capacities obtained for the four solid compounds were corrected by a program that includes the calibration of temperature and power scales of our DSC-2C. These values were fitted by a least-squares method. Due to the temperature interval being restricted, the molar heat capacities may be expressed as a function of temperature by the equation

$$C_{\text{p,m}}/\text{J K}^{-1}\,\text{mol}^{-1} = a + b(T/K) + c(T/K)^2 \qquad (3)$$

In Table 5 are listed the interval of temperature, ΔT, on which the measurements were done, the parameters a, b, and c, and the coefficients of determination R^2 for the four compounds.

The standard molar enthalpies of formation for both crystalline and gaseous phases, and the standard molar enthalpies of sublimation for each of the four compounds at $T = 298.15$ K, are reported in Table 6.

No vapor pressures or combustion enthalpies of *N*-methylmaleimide, *N*-methylsuccinimide, *N*-methylphthalimide, and *N*-benzoyl-*N*-methylbenzamide have been found in the literature for comparison with our results.

Discussion

We recall the recent discussion of the enthalpy of Diels−Alder reactions involving maleic anhydride and *N*-methylmaleimide as competing dienophiles.[5,10] With furan and 1,3-diphenylisobenzofuran as the dienes—and leaving aside questions of *endo*/*exo* adduct ratios—the differences are ca. 13 and 17 kJ mol^{-1}, respectively. It may be argued that these reactions ultimately relate to saturation of the formal C=C bond and with this, all conjugation to the imide and thus antiaromatic destabilization ceases.

As such, somewhat more direct, and thus simpler, is the comparison of the enthalpy of hydrogenation to the corresponding succinimides and succinic anhydride relative to that of cyclopentene and other species with five-membered rings—we recognize this as paralleling the understanding of the aromaticity of benzene in terms of the enthalpy of hydrogenation of benzene relative to those of cyclohexene and other species with six-membered rings. Because the enthalpy of formation of hydrogen is 0.0 by definition, the enthalpy of hydrogenation of an arbitrary compound is the difference of its enthalpy of formation and that of its hydrogenated product. In particular, the enthalpy of hydrogenation of *N*-methylmaleimide is precisely the difference of its enthalpy of formation and that of *N*-methylsuccinimide. From numbers presented in the current paper, the difference is found to be 136.7 ± 2.2 kJ mol^{-1}. Using enthalpies of formation from the archival and current literature,[11] the enthalpy of hydrogenation of maleic anhydride is likewise 129.6 ± 5.4 kJ mol^{-1}. By contrast, the enthalpies of hydrogenation of the obviously “unconjugated” cyclopentene and “merely conjugated” cyclopentadiene (to cyclopentene) are 110.3 ± 1.6 and 100.4 ± 2.1 kJ mol^{-1}. If it is argued that the 110.3−100.4 ≈ 10 kJ mol^{-1} difference between the hydrogenation enthalpy values for cyclopentene and cyclopentadiene reflects the conjugation energy of the latter species, then the 110.3−136.7 ≈ −26 and 110.3−129.6 ≈ −19 kJ mol^{-1} reflect the antiaromatic destabilization of *N*-methylmaleimide and maleic anhydride.

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(9) Rihani, D. N.; Doraiswamy, L. K. *Ind. Eng. Chem.* **1965**, *8*, 17.

(10) These two results are from ref 5. Encouragingly, much the same difference is derivable from reactions of 1,3-diphenylbenzoisofuran with maleic anhydride and a whole series of variously substituted *N*-phenylmaleimides, cf.: Kiselev, V. D.; Ustyugov, A. N.; Breus, I. P.; Konovalov, A. I. *Dokl. Chem.* **1977**, *234*, 320.

(11) The enthalpy of formation of maleic anhydride is taken from Pedley, *op. cit.*, while that of succinic anhydride (−527.9 ± 1.7 kJ mol^{-1}) is from the following: Yang, M.-Y.; Pilcher, G. *J. Chem. Thermodyn.* **1990**, *22*, 893.

Table 5. Parameters of Eq 3 for the Molar Heat Capacities $C_{p,m}$

compound	ΔT/K	a	b	c	R^2
N-methylmaleimide	270−339	-3.2957×10^2	2.8373	-4.1621×10^{-3}	99.32
N-methylsuccinimide	270−339	-2.5978×10^2	2.2906	-3.0740×10^{-3}	99.50
N-methylphthalimide	270−339	-2.5532×10^2	2.2665	-2.6241×10^{-3}	99.66
N-benzoyl-*N*-methylbenzamide	270−363	2.9212×10^2	−0.9812	3.2761×10^{-3}	99.64

Table 6. Standard Molar Enthalpies of Formation $\Delta_f H°_m$(cr) and of Sublimation $\Delta_{sub}H°_m$ of the Solid and $\Delta_f H°_m$(g) of the Gas at $T = 298.15$ K and $p^0 = 101.325$ kPa

compound	$\Delta_f H°_m$(cr)/ (kJ mol^{-1})	$\Delta_{sub}H°_m$/ (kJ mol^{-1})	$\Delta_f H°_m$(g)/ (kJ mol^{-1})
N-methylmaleimide	-329.3 ± 1.4	73.3 ± 0.5	-256.0 ± 1.5
N-methylsuccinimide	-469.8 ± 1.6	80.1 ± 0.3	-389.7 ± 1.6
N-methylphthalimide	-325.0 ± 2.1	91.1 ± 0.5	-233.9 ± 2.2
N-benzoyl-*N*-methylbenzamide	-239.6 ± 3.8	120.1 ± 0.4	-119.5 ± 3.8

Taking all of the numbers literally (i.e., by ignoring error bars), we would conclude that the maleimide is more destabilized, and thus more antiaromatic, than is maleic anhydride by ca. 7 kJ mol^{-1}. This result is in satisfactory agreement with the ca. 11 kJ mol^{-1} difference for maleic anhydride and the parent maleimide given by quantum chemical calculations[5] at both the HF/6-31G* and MP2/6-31G*//HF/6-31G* levels. It also follows from the general conclusion that if pyrrole is more aromatic than furan, the corresponding diones are sensibly antiaromatic in the reverse order.[12]

It has long been recognized[13] that benzoannelation of a relatively unstrained, unconjugated olefin is accompanied by a ca. 28 kJ mol^{-1} increase in the enthalpy of formation. For example, the formal transformation of (*Z*)-2-butene and cyclopentene to *o*-xylene and indane show changes of 26.2 ± 1.5 and 26.8 ± 2.2 kJ mol^{-1}. Even the "merely" conjugated cyclopentadiene and the resultant indene show the comparable difference of 29.1 ± 2.6 kJ mol^{-1}. By contrast, benzoannelation of the aromatic benzene to form naphthalene shows a much larger, more positive difference, 67.7 ± 1.7 kJ mol^{-1}. Intuitively, we might think that benzoannelation of destabilized or even antiaromatic species should show a smaller, less positive, difference than the unstrained, unconjugated olefins. We find for the benzoannelation of *p*-benzoquinone and 1,4-naphthoquinone results in differences of 25.4 ± 4.0 and 21.8 ± 3.5 kJ mol^{-1}, respectively, showing but a small effect of benzoannelation for destabilized species. Indeed, the transformation of maleic anhydride into phthalic anhydride gives an enthalpy of formation change of 26.9 ± 5.5 kJ mol^{-1} while the difference for the *N*-methyl derivatives of maleimide and phthalimide is 22.1 ± 2.7 kJ mol^{-1}. This analysis suggests maleic anhydride and maleimides are not aromatic, but distressingly little else has been learned.

Using a recent Dewar/Breslow related model of aromaticity and antiaromaticity,[14] the destabilization of maleic anhydride may be ascertained using the difference of its enthalpy of formation and that of benzoic anhydride. The former difference is 79.3 ± 6.8 kJ mol^{-1}, some 8 kJ mol^{-1} less than the ca. 87 kJ mol^{-1} derived from the difference of the enthalpies of formation of cyclopentene and 1,3-diphenylpropane.[15] This suggests maleic anhydride is destabilized by 8 kJ mol^{-1}. Relatedly, the difference of the enthalpies of formation of *N*-methylmaleimide and *N*-benzoyl-*N*-methylbenzamide provides for the destabilization for the former. From our numbers for both imides, the difference is found to be 136.5 ± 4.1 kJ mol^{-1}, which, taken at face value, suggests *N*-methylmaleimide is stabilized by ca. 50 kJ mol^{-1}. We find stabilization, much less of this magnitude, to be quite inconceivable: What is the origin of the discrepancy? Is it our measured enthalpy of formation of *N*-benzoyl-*N*-methylbenzamide that is problematic? To first approximation we should think that the following "formal" phenyl/methyl exchange reaction should be approximately thermoneutral.

$$C_6H_5N(COCH_3)_2 + (C_6H_5CO)_2O + CH_3NH_2 \rightarrow CH_3N(COC_6H_5)_2 + (CH_3CO)_2O + C_6H_5NH_2 \quad (4)$$

From the archival and our newly measured gas phase enthalpies of formation (see Table 6), the preceding reaction is found to be ca. 10 kJ mol^{-1} endothermic in rough accord with our expectations. The enthalpies of formation of the other imides were earlier shown to be consistent as well. As we are not yet ready to jettison the model presented in ref 14 because of its successes with aromaticity, we leave our measured values and derived analyses intact. In doing so, we leave ambiguous the degree of antiaromaticity, and merely even of the degree of destabilization, of maleic anhydride and the various maleimides.

Conclusion

Variously N-substituted maleimides and maleic anhydride are well-established to be highly reactive species in Diels−Alder, ring-opening, and nucleophilic addition reactions. This has been earlier ascribed to their antiaromaticity. Our thermochemical measurements show this antiaromaticity to be quite modest.

Experimental Section

Materials. *N*-Methylmaleimide was prepared according to the literature procedure[16] by the reaction of maleic anhydride (0.1 mol) with methylamine (0.1 mol) at 0 °C for 1 h, followed by cyclization of the resultant *N*-methylmaleamic acid by heating with excess acetic anhydride in the presence of sodium acetate (0.05 mol) in a steam bath for 1 h. The product, obtained in 60% yield, was recrystallized three times from

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[12] This parallels customary assumptions as to the relatively greater aromatic stabilization of benzene over naphthalene and the relatively greater destabilization of *p*-benzoquinone over 1,4-naphthoquinone.

[13] See, for example, the use of this regularity in the following: Liebman, J. F. *The Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983.

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[15] The needed enthalpy of formation of gaseous 1,3-diphenylpropane was derived in two ways: summing the enthalpy of formation for the liquid (Serijan, K. T.; Wise, P. H. *J. Am. Chem. Soc.* **1951**, *73*, 4766) with an estimated enthalpy of vaporization using the simple equation of Chickos, J. S.; Hyman, A. S.; Ladon, L. H.; Liebman, J. F. *J. Org. Chem.* **1981**, *46*, 4294, and by summing the archival enthalpy of formation of 1,2-diphenylethane and the "universal methylene increment" (or ca. −20.6 kJ mol^{-1}) discussed in the following: Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

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diethyl ether to obtain colorless crystals: mp 96 °C (lit.[16] mp 96 °C); ^{1}H NMR (CDCl$_3$) δ 3.0 (s, 3 H, CH$_3$), 6.67 (s, 2 H, CH); MS (70 eV) *m/e* 111 (M$^+$, 100), 83 (M$^+$ − CO, 23), 82 (24), 54 (87).

***N*-Methylsuccinimide** was purchased from Aldrich Chemical Co. and was recrystallized three times from a mixture of diethyl ether−petroleum ether (bp 40−60 °C) into colorless needles: mp 71 °C (lit.[17] mp 71 °C); ^{1}H NMR (CDCl$_3$) δ 2.73 (s, 4 H, CH$_2$), 2.99 (s, 3 H, N-Me).

***N*-Methylphthalimide** was prepared according to the literature procedure[18] by condensation of phthalic anhydride (0.1 mol) with 33% aqueous methylamine (0.15 mol), followed by removal of water by azeotroping with toluene, using a Dean−Stark apparatus. The product, obtained in 91% yield, was recrystallized from ethyl alcohol into colorless needles: mp 134 °C (lit.[18] mp 134 °C); ^{1}H NMR (CDCl$_3$) δ 3.19 (s, 3 H, Me), 7.7−7.84 (m, 4 H, Ar-H).

***N*-Benzoyl-*N*-methylbenzamide**[19,20] was prepared by the reaction of benzoyl chloride with *N*-(phenylmethylene)methanamine *N*-oxide with benzoyl chloride as follows:

***N*-(Phenylmethylene)methanamine *N*-Oxide.**[19] Benzaldehyde (9.7 g, 0.091 mol) was placed in a 250-mL three-necked flask, and 9.6 g (0.115 mol) of *N*-methylhydroxylamine hydrochloride in 145 mL of methylene chloride was added. Sodium bicarbonate (24.1 g, 0.287 mol) was added with stirring. The reaction mixture was refluxed for 15 h. The reaction mixture was cooled in an ice bath and filtered to remove salt. The filtrate was evaporated under reduced pressure, 20 mL of hexanes was added to the residue, and the mixture was cooled in an ice bath. The solid precipitated was filtered and washed with hexanes to give a pale yellow solid (6.5 g, 53%): mp 79−81 °C (lit.[19,20] mp 82−84 and 84−86 °C); ^{1}H NMR (CDCl$_3$) δ 3.86 (s, 3 H, Me), 7.39 (m, 4 H, Ar-H), 8.22 (m + s, 2 H, Ar-H + N=CH).

***N*-Benzoyl-*N*-methylbenzamide.**[21] In a 250-mL three-necked flask were placed 2.7 g (0.02 mol) of *N*-(phenylmethylene)methanamine *N*-oxide and 2.2 g (0.022 mol) of triethylamine in 160 mL of dry dioxane. Benzoyl chloride (3.1 g, 0.022 mol) was added dropwise at room temperature during a period of 5 min. Triethylamine hydrochloride began to precipitate within minutes. The reaction mixture was stirred overnight at room temperature. The amine hydrochloride salt was removed by filtration, and the filtrate was evaporated under reduced pressure. The solid residue was recrystallized from ethanol three times to obtain colorless crystals: mp 90−92 °C (lit.[21] mp 90−92 °C); ^{1}H NMR (CDCl$_3$) δ 3.52 (s, 3 H, Me), 7.23 (m, 6 H, Ar-H), 7.46 (m, 4 H, Ar-H).

Procedure for Thermochemical Measurements. Control of purity, as assessed by differential scanning calorimetry (DSC) and the fractional fusion technique,[22a] indicated that the mole fraction impurities in each compound was <0.001. The samples were studied by DSC[22b] over the whole working temperature range, and no phase transitions in the solid state were observed.

The combustion experiments of the four compounds were performed with a static bomb calorimeter. Apparatus and procedure have been described in ref 23.

Table 7. Physical Properties at 298.15 K (Values in Parentheses Were Estimated)

compound	M/ (g mol^{-1})	ρ/ (g cm^{-3})	$(\delta u/\delta p)_T$/ (J kPa^{-1} g^{-1})	c_p/ (J K^{-1} g^{-1})
polyethylene	13.558	0.918	(−0.00023)	2.0
N-methylmaleimide	111.100	1.30	(−0.00010)	1.32
N-methylsuccinimide	113.116	1.34	(−0.00008)	1.33
N-methylphthalimide	161.160	1.37	(−0.00008)	1.15
N-benzoyl-*N*-methylbenzamide	239.274	1.26	(−0.00009)	1.20

The energy of combustion of the compounds was determined by burning the solid sample in pellet form in oxygen in a bomb with 1 cm^3 of water added. Due to the relatively high vapor pressure of the *N*-methylsuccinimide, *N*-methylmaleimide, and *N*-benzoyl-*N*-methylbenzamide, the pelleted compounds were burnt enclosed in polyethylene bags. The combustion bomb was flushed and filled with oxygen, previously freed from combustible impurities, up to a pressure of 3.04 MPa, at T = 298.15 K. The initial temperature was 296.95 K. The energy of reaction was always referred to the final temperature 298.15 K.

The energy equivalent of the calorimeter was determined from the combustion of benzoic acid, NIST standard reference sample 39i, having a specific energy of combustion under the conditions specified on certificate of $-(26434 \pm 3)$ J g^{-1}. Three values of the energy equivalent of the calorimeter were used in computing the combustion experiments: ϵ(calor) = (14299.9 ± 1.5) J K^{-1} for *N*-methylsuccinimide, ϵ(calor) = (14288.5 ± 2.3) J K^{-1} for *N*-methylmaleimide and *N*-methylphthalimide, and ϵ(calor) = (14306.5 ± 1.5) J K^{-1} for *N*-benzoyl-*N*-methylbenzamide from 15, 12, and 15 experiments respectively, where the uncertainties quoted are the standard deviations of the means. The specific energy of combustion and empirical formula of polyethylene are $-(46371 \pm 4)$ J g^{-1} and $C_{0.961}H_{2.000}$.[24] The corrections for nitric acid formation were based on −59.7 kJ mol^{-1} for the molar energy of formation of 0.1 mol dm^{-3} HNO$_3$(aq) from N$_2$(g), O$_2$(g), and H$_2$O(l). All samples were weighed with a Mettler AT-21 microbalance. For the correction of apparent mass to mass, conversion of the energy of the actual bomb process to that of the isothermal process, and correction to standard states, we have used the values of density ρ, specific heat capacity c_p, and $(\delta u/\delta p)_T$, respectively, as given in Table 7.

The densities were measured in our laboratory. Heat capacities were determined by DSC. Corrections to standard states were made according to suggestions by Hubbard et al.[25] The atomic weights of the elements were those recommended by IUPAC in 1991.

A Perkin-Elmer DSC-2C, connected to a Model 3600 Data Station and provided with an Intracooler-2 unit, was used for the DSC measurements. Its temperature scale was calibrated by measuring the melting point of the recommended high-purity standards: *n*-octadecane, *n*-octadecanoic acid, benzoic acid, indium, and tin.[22b] The power scale was calibrated using high-purity indium (>99.999 mol % of In). Heat capacities were determined as in ref 26. Synthetic sapphire and benzoic acid were used as standard materials.[22c] The complete temperature range for determination of the heat capacities was divided into two intervals for *N*-methylmaleimide, *N*-methylsuccinimide, *N*-methylphthalimide, and three intervals for *N*-benzoyl-*N*-methylbenzamide of approximately 40 K, overlapping by 15 K from one interval to another. The heat

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capacity values were the average of five experiments done for every interval of temperature. Fresh samples of mass ~10 mg were scanned using a heating rate of 0.17 K s^{-1} and a sensitivity of 0.008 W full scale. The estimated error of the molar heat capacities was between $0.01C_{p,m}$ and $0.02C_{p,m}$.

The vapor pressures for the four compounds were measured by the Knudsen effusion method as previously described.[27ab] The effusion orifice area, a, and the Clausing coefficient,[27c] W_a, were $a = (3.47 \pm 0.02) \times 10^{-3}$ cm^2 and $W_a = (0.94 \pm 0.01)$ for *N*-methylsuccinimide, *N*-methylphthalimide, and *N*-benzoyl-*N*-methylbenzamide, and $a = (0.799 \pm 0.03) \times 10^{-3}$ cm^2 and $W_a = (0.958 \pm 0.009)$ for *N*-methylmaleimide, respectively. The enthalpies of sublimation were computed from standard relations between pressure and temperature.

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