Table 1 gives a comparison of our results α_1 for the 1s-state with Latter's results [4] for several Z-values.

Z	8	10	13	19	26	29	37	47	57	65	74	82	92
(a)	6.092	—	10.536	16.022	22.546	25.365	32.939	42.485	51.971	59.800	68.498	76.250	85.965
(b)	5.897	7.680	10.260	15.962	22.455	25.404	33.048	42.672	52.347	59.785	68.348	76.722	85.769

Table 1. A comparison of our results (b) with Latter's results (a) for the 1s-state and several Z-values.

Table 2 shows a comparison of our approximate eigenvalues α_1 for $Z=80$ with the corresponding Hartree eigenvalues for several quantum numbers.

States	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
α_1 Eq. (7)	74.728	30.794	30.348	15.218	14.713	13.702	7.521	7.041	6.079	4.638
Hartree	74.48	30.41	29.87	14.76	14.19	13.08	6.87	6.34	5.27	3.09

Table 2. A comparison of our approximate eigenvalues α_1 given by Eq. (7) for $Z=80$ with the corresponding Hartree-values.

Table 1 and 2 show that the approximate eigenvalues calculated by help of Eq. (7) give reasonable results. In order to obtain more accurate eigenvalues than those given by α_1 we must solve a determinant of higher order than that in Eq. (6). The corresponding eigenfunctions for practical purpose are obtained from Eqs. (2) and (5) by respecting only finite numbers of the coefficients c_{n-l-1} so that the eigenfunctions show the proper numbers of zeroes. Eq. (2) shows that the eigenfunctions have accurate behavior for $r=0$ and $r\to\infty$.

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Reactivity Indices in Benzotropones

L. Klasinc

Kernforschungszentrum Karlsruhe, Institut f. Strahlenchemie, Karlsruhe, Germany

and Z. Majerski and N. Trinajstić

Institute "Rudjer Bošković", Zagreb, Croatia, Yugoslavia

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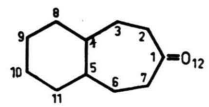
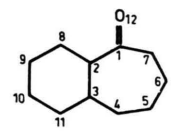
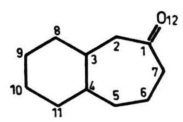
The present communication reports a theoretical study of the reactivity indices of tropones fused with a benzene ring; the so-called benzotropones. There are three possible benzotropones: 4,5-benzotropone, 2,3-benzotropone, and 3,4-benzotropone, shown in Fig. 1. Several research workers [1–9] have reported the syntheses and properties of 4,5-benzotropone and 2,3-benzotropone. To our knowledge there is so far no synthesis of 3,4-benzotropone reported in literature. We have investigated these molecules regarding substitution and addition reactions, being interested in predict-



4,5- BENZOTROPONE (I)



2,3 - BENZOTROPONE (II)



3,4 - BENZOTROPONE (III)

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ing the positions of electrophilic, radical, or nucleophilic attack. In doing this we examine the properties of the molecular orbitals of the initial compounds or in other words we have followed the *isolated-molecule approximation* [10]. In this approximation we can expect a correlation between the electron density and the attacking charged species. Since the radical species are neutral the correlation with the free valence proved to be quite successful. It is also possible to correlate the reactivity of the bond with the bond order value, and predict the most reactive bonds.

We have therefore applied the molecular orbital theory in the frame-work of the HÜCKEL method [11, *] in order to calculate the π-bond orders (Table 1), the π-electron densities, the free valence indices, the superdelocalizabilities, and the frontier electron densities (Table 2). The predictions of reactivity are given in Table 3. These predictions are based on three groups of quantities: 1. the π-charge densities, the π-bond orders, and the free valence indices; 2. the superdelocalizabilities; and 3. the frontier electron densities **.

I		II		III	
Bond	p_{ij}	Bond	p_{ij}	Bond	p_{ij}
1— 2	0.371	1— 2	0.335	1— 2	0.426
2— 3	0.821	1— 7	0.380	1— 7	0.408
3— 4	0.466	2— 3	0.560	2— 3	0.659
4— 5	0.539	2— 8	0.631	3— 4	0.452
4— 8	0.596	3— 4	0.476	3— 8	0.516
8— 9	0.690	3—11	0.587	4— 5	0.615
9—10	0.633	4— 5	0.768	4—11	0.534
1—12	0.799	5— 6	0.526	5— 6	0.602
		6— 7	0.793	6— 7	0.737
		8— 9	0.679	8— 9	0.747
		9—10	0.638	9—10	0.573
		10—11	0.694	10—11	0.740
		1—12	0.808	1—12	0.756

Table 1. π-bond orders.

Compound	Position	q	F	S_e	S_r	S_n	D_e	D_r	D_n
I	1	0.796	0.191	0.296	0.507	0.718	0.023	0.012	0.000
	2	1.015	0.540	1.104	0.865	0.625	0.397	0.431	0.464
	3	0.919	0.445	0.746	0.920	1.095	0.073	0.108	0.143
	4	0.982	0.131	0.749	0.655	0.562	0.202	0.212	0.222
	8	0.987	0.446	0.901	0.947	0.993	0.015	0.022	0.028
	9	0.985	0.409	0.843	0.799	0.755	0.136	0.139	0.143
	12	1.429	0.933	0.903	0.457	0.012	0.332	0.166	0.000
II	1	0.791	0.210	0.299	0.508	0.718	0.021	0.026	0.030
	2	1.002	0.207	0.840	0.820	0.800	0.087	0.099	0.111
	3	0.974	0.111	0.682	0.685	0.689	0.060	0.045	0.030
	4	0.942	0.488	0.955	0.892	0.829	0.328	0.397	0.467
	5	0.985	0.438	0.974	0.745	0.516	0.322	0.274	0.226
	6	0.924	0.413	0.713	0.884	1.056	0.064	0.144	0.225
	7	1.025	0.559	1.242	0.851	0.460	0.504	0.486	0.468
	8	0.977	0.423	0.830	0.841	0.853	0.051	0.045	0.040
	9	0.989	0.415	0.888	0.787	0.686	0.178	0.178	0.177
	10	0.980	0.400	0.789	0.846	0.903	0.000	0.000	0.000
	11	0.990	0.451	0.944	0.848	0.752	0.173	0.178	0.183
	12	1.422	0.925	0.893	0.508	0.123	0.210	0.127	0.044
III	1	0.823	0.143	0.384	0.459	0.533	0.049	0.025	0.000
	2	0.980	0.647	1.505	1.459	1.412	0.476	0.504	0.531
	3	0.957	0.106	0.618	0.799	0.881	0.003	0.021	0.038
	4	0.972	0.131	0.726	0.810	0.893	0.042	0.057	0.071
	5	0.922	0.516	1.078	1.273	1.468	0.281	0.338	0.394
	6	0.948	0.394	0.713	0.849	0.984	0.000	0.008	0.015
	7	0.961	0.588	1.213	1.413	1.612	0.278	0.354	0.430
	8	0.997	0.469	1.106	0.978	0.849	0.213	0.194	0.175
	9	0.977	0.412	0.849	0.911	0.974	0.059	0.072	0.085
	10	0.984	0.419	0.932	0.904	0.877	0.132	0.128	0.123
	11	0.988	0.458	1.016	0.963	0.910	0.153	0.145	0.138
	12	1.492	0.976	1.261	0.418	0.425	0.313	0.157	0.002

Table 2. Reactivity indices. q is the π-electron density, F the free valence, S the superdelocalisability, and D the frontier electron density (e: electrophilic, r: radical, n: nucleophilic).

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* The assumption was made that all three investigated molecules are planar. The following empirical parameters were used in the calculations: $\alpha_0=\alpha_c+1.20\,\beta_{cc}$, $\alpha_1=\alpha_c-0.040\,\beta_{cc}$, $\alpha_2=\alpha_c$, and $\beta_{c0}=2.00\,\beta_{cc}$, respectively.

** Although there are no experimental data for 3,4-benzotropone, we have for the sake of completness included in the Tables its theoretical results.

Compound	Attack			
	electrophilic	nucleophilic	radical	addition
I	2,7 > 8,11 [a] 2,7 > 8,11 [b] 2,7 > 9,10 [c]	3,6 > 9,10 [a] 3,6 > 8,11 [b]	2,7 > 8,11 [a] 8,11 > 3,6 [b]	2–3,6–7 [a]
II	7 > 11 > 9 [a] 7 > 11 > 5 [b] 7 > 4 > 5 [c]	6 > 4 > 8 [a] 6 > 10 > 8 [b]	7 > 11 > 4 [a] 4 > 6 > 7 [b]	6–7 > 4–5 [a]
III	8 > 11 > 10 [a] 2 > 7 > 8 [b] 2 > 5 > 7 [c]	5 > 6 > 7 [a] 7 > 5 > 2 [b]	2 > 7 > 5 [a] 2 > 7 > 5 [b]	8–3 > 6–7 [a]

Table 3. The prediction of reactivity. [a] Prediction based on the charge densities, bond orders, and free valence indices; [b] prediction based on the superdelocalisabilities; [c] prediction based on the frontier electron densities.

Positions 2 and 7 in 4,5-benzotropone (2-chloro-4,5-benzotropone [12], 2-acetyl-4,5-benzotropone [13], 2,7-dibenzoyl-4,5-benzotropone [14]) and position 7 (or 5) in 2,3-benzotropone (7-chloro-2,3-benzotropone [4], 5,7-dibromo-2,3-benzotropone [9], 5,7-dinitro-2,3-benzotropone [9]) are the most reactive sites for electrophilic reagents. Positions 3 and 6 in 4,5-benzotropone and position 6 (or 4) in 2,3-benzotropone (4-hydroxy-2,3-benzotropone [15]) are the possible sites for nucleophilic attack. Positions 2 and 7 (or 8 and 11) in 4,5-benzotropone (2,7-dimethyl-4,5-benzotropone [7, 8, 16–19], 2,7-diethyl-4,5-benzotropone [16], 2-methyl-4,5-benzotropone [7, 20–22], 2,7-dialkyl-4,5-benzotropone [21]) and position 7 (or 4) in 2,3-benzotropone (5,7-dialkyl-2,3-benzotropone [21]) are the most reactive positions for radical attack. The most reactive bonds for addition reactions in all of the three investigated compounds are the bonds next to that carbon atom in the tropone ring which is bonded to oxygen.

Finally we want to point out that the coincidence of these predictions based on three different groups of quantities is not surprising since all these are derived from the Hückel coefficients and because of that they are not independent quantities and therefore all lead to similar predictions for the positions of attack.

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