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Molecular Docking Studies in Organic Photoconductors: The Chlorodiane Blue and *p*-(Diethylamino)benzaldehyde Diphenylhydrazone Interface

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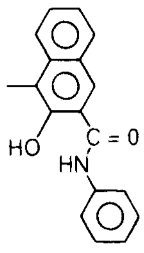
Molecular docking studies are reported for chlorodiane blue (CDB) and *p*-(diethylamino)benzaldehyde diphenylhydrazone (DEH), two molecules that make up the interface between the carrier generation and carrier transport layers in organic photoconductors. The docking studies reveal strong interactions and close contacts between the diphenylhydrazone and diethylaniline groups in DEH with the phenylamido and hydrazone–quinone groups in CDB.

Introduction

Layered organic photoconductors are widely employed as the photosensitive element in printers and photocopiers. Photoconduction is achieved by conduction of charges across a dielectric medium under illumination and an applied electric field. The process is illustrated in Figure 1. The charges are initially generated by photoexcitation of a carrier generation layer that contains a photosensitive dye such as chlorodiane blue. After injection of holes into charge transport molecules such as *p*-(diethylamino)benzaldehyde diphenylhydrazone (DEH), the charges traverse the dielectric and subsequently annihilate the surface ions. These processes must occur with a high enough efficiency to help meet the transit time requirements imposed by printers and copiers to ensure rapid output of printed material. Consequently, photoconduction critically depends upon the integrity of the interface between the carrier-generation (CGL) and carrier-transport layers (CTL) and any chemical changes that take place at the interface during the electrophotographic cycle will have deleterious effects on the virgin electrical properties of the photoconductor. For example, in a photoconductor composed of chlorodiane blue (CDB) and *p*-(diethylamino)benzaldehyde diphenylhydrazone (DEH), exposure of CDB to long-wavelength light initiates a solid-state photochemical reaction, apparently with DEH, resulting in bleaching and depletion of the dye at the interface.[1,2] The photoconductor loses its ability to generate and/or inject carriers upon photoexcitation in an electrical field and is considered to be "electrically fatigued". Thus the relative orientation of one molecule to another, for example, CDB to DEH at the CGL/CTL interface, can significantly affect the efficiency with which charge transfer occurs[3] as well as of the photochemically induced reaction that ensues.[1,2] It is therefore clear that studies on the CDB/DEH interface would be significantly beneficial, and one method by which insight may be gathered is via molecular modeling. Therefore, in this report, we investigate the molecular docking of DEH on CDB. The non-bond-interaction energy between CDB and DEH is evaluated and used as a guide to determine the preferred intermolecular orientation. The docked structures with the lowest intermolecular interaction or non-bond energies are considered to be representative of the most favorable structure formed between DEH and CDB. The results of the docking studies presented here identify close contact intermolecular distances between the diphenylhydrazone and diethylaniline structural moieties in DEH and the phenylamido and hydrazone–quinone groups in CDB.



Napthol AS
Coupling Component

Computational Details

For molecular docking studies, the Biosym Insight & Discover computer modeling software[4] was used. The potential energy used in these studies was of the form shown in eq 1, where the contributions to energy come from [1] bond stretching, [2] bond angle bends, [3] rotation of torsion angles, [4] out-of-plane deformation, [5]–[9] cross terms, i.e., bond–bond, angle–angle, bond–angle, torsion–torsion, and out-of-plane bending, [10] van der Waals interaction with a Lennard-Jones function, and [11] electrostatic potential. Molecular docking studies of DEH on CDB were performed by evaluation of the non-bond-interaction energy between DEH and CDB to determine the preferred intermolecular orientation. The non-bond potential is composed of two parts, the van der Waals and the electrostatic potentials (eq

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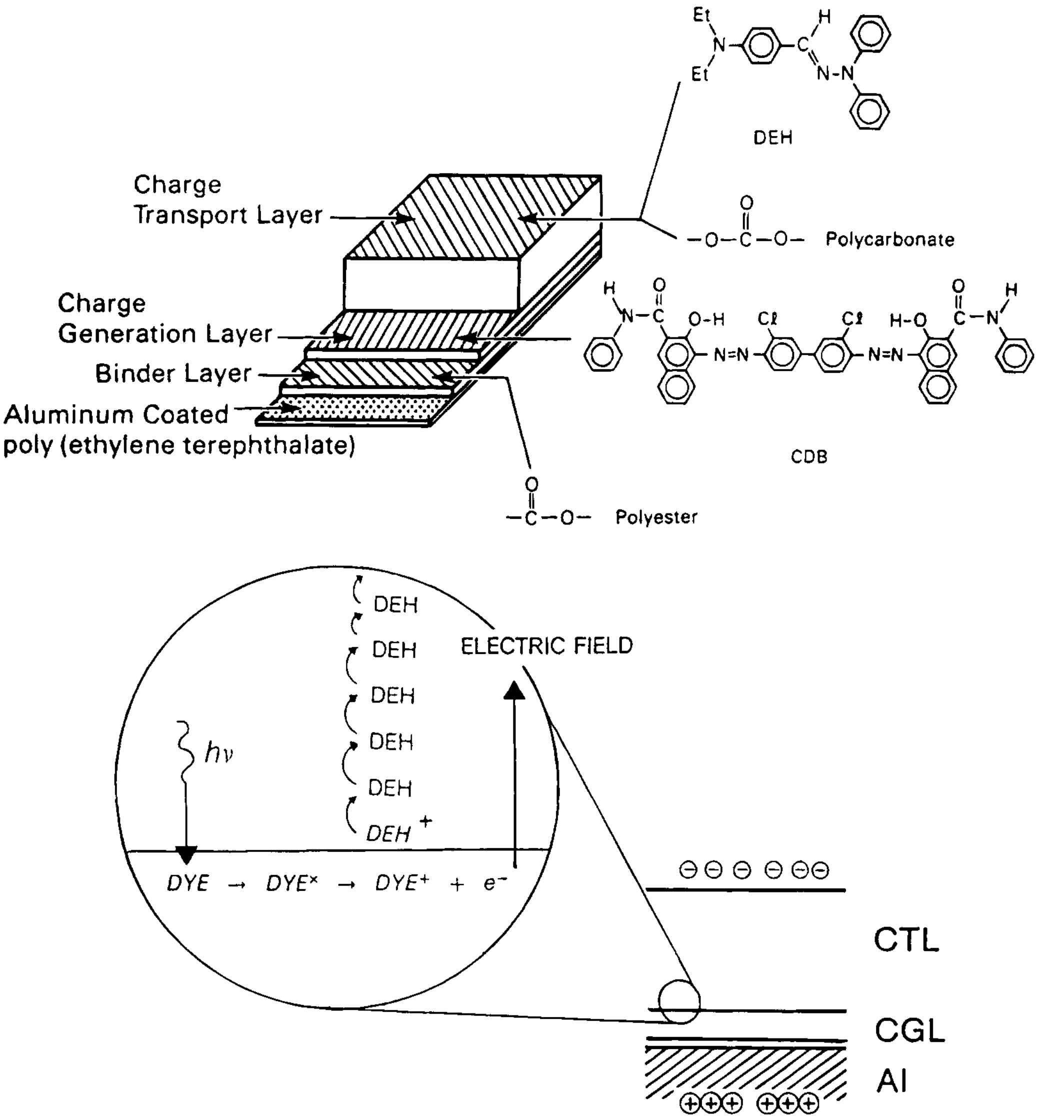

Figure 1. Top: compositional profile of an organic photoconductor. Bottom: illustration of the photoconduction process. CTL is the charge-transport layer; CGL is the charge generation layer.

$$
\begin{aligned}
E = {} & \underbrace{\sum_b D_b[1 - e^{-\alpha(b-b_0)^2}]}_{[1]} + \underbrace{\sum_\theta H_\theta(\theta - \theta_0)^2}_{[2]} + \\
& \underbrace{\sum_\phi H_\phi[1 + s\cos(n\phi)]}_{[3]} + \underbrace{\sum_\chi H_\chi \chi^2}_{[4]} + \\
& \underbrace{\sum_b \sum_{b'} F_{bb'}(b - b_0)(b' - b_0')}_{[5]} + \\
& \underbrace{\sum_\theta \sum_{\theta'} F_{\theta\theta'}(\theta - \theta_0)(\theta' - \theta_0')}_{[6]} + \\
& \underbrace{\sum_b \sum_\theta F_{b\theta}(b - b_0)(\theta - \theta_0)}_{[7]} + \\
& \underbrace{\sum_\phi F_{\phi\theta\theta'} \cos\phi(\theta - \theta_0)(\theta' - \theta_0')}_{[8]} + \\
& \underbrace{\sum_\chi \sum_{\chi'} F_{\chi\chi'}\chi\chi'}_{[9]} + \underbrace{\sum \epsilon[(r^*/r)^{12} - 2(r^*/r)^6]}_{[10]} + \underbrace{\sum q_i q_j/\epsilon r_{ij}}_{[11]} \qquad (1)
\end{aligned}
$$

2). The van der Waals energy is described by a 6−12 non-bond potential while evaluation of the electrostatic energy requires knowledge of the atomic charges on CDB and DEH:

$$E_{\text{inter}} = \sum_i \sum_j \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{\epsilon r_{ij}} \qquad (2)$$

where E_{inter} is the non-bond intermolecular interaction energy, q_i and q_j are the charges on the ith and jth atom, ϵ is the dielectric constant, and r_{ij} is the distance between atoms i and j. A_{ij} and B_{ij} are parameters.[4]

Initially, both DEH and half of the CDB structure, HCDBH, were optimized via ab initio Hartree−Fock calculations using the 3-21G basis set[5] to provide reference structures for the isolated molecules. The ab initio calculations were performed using the Mulliken system of computer codes.[6] The individual optimized

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(5) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(6) *Mulliken*, Rice, J. E.; Horn, H.; Lengsfield, B. H.; McLean, A. D.; Carter, J. T.; Replogle, E. S.; Barnes, L. A.; Maluendes, S. A.; Lie, G. C.; Gutowski, M.; Rudge, W. E.; Sauer, S. P. A.; Lindh, R.; Andersson, K.; Chevalier, T.; Widmark, P.-O.; Bouzida, D.; Pacansky, G.; Singh, K.; Gillan, C. J.; Carnevali, P.; Swope, W. C.; Liu, B. Almaden Research Center, IBM Research Division, 6500 Harry Road, San Jose, CA 95120-6099.

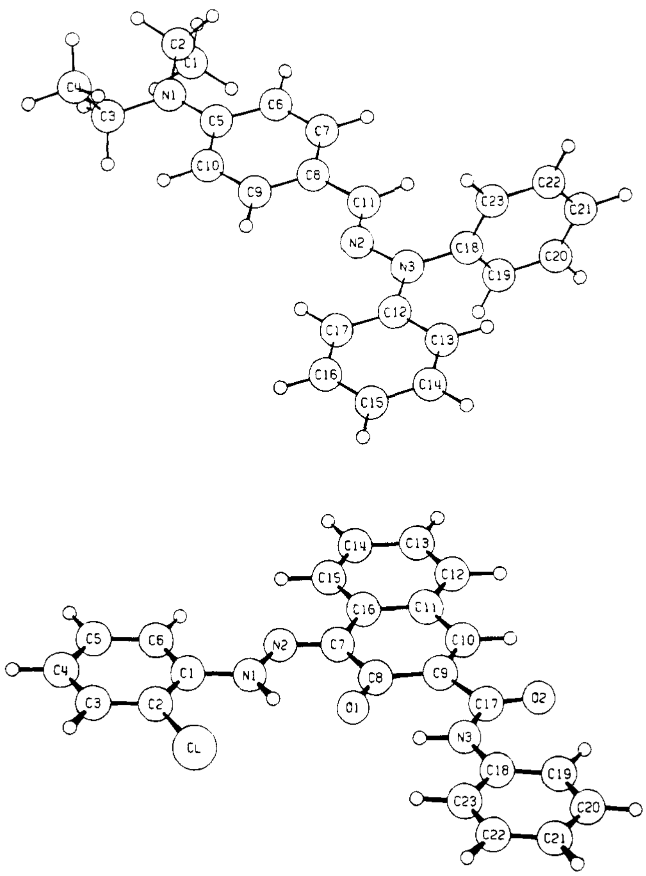

Figure 2. HF/3-21G optimized geometries for DEH (top) and HCDBH (bottom). Total energies are −1 042.989 448 and −1 644.004 699 hartrees for DEH and HCDBH, respectively.

geometries are presented in Figure 2. The half CDB molecule is planar. The DEH molecule has an extensive π plane from the diethylaniline amine nitrogen atom to a phenyl group of the diphenylhydrazone portion of the molecule. The other diphenylhydrazone phenyl group is nearly perpendicular to the π plane. The two ethyl groups bonded to the aniline amine nitrogen atom are "trans" to one another. The ab initio structure for DEH is consistent with the crystal geometry.[7]

The ab initio chemical structures of both DEH and chlorodiane blue were then individually minimized via molecular mechanics using the Biosym CVFF force field. The hydrazone–quinone form of chlorodiane blue (as opposed to azo–enol) was exclusively considered because of its relevance to photocarrier generation.[8] Docking studies were then performed by moving DEH relative to a stationary chlorodiane blue (CDB) and identifying the docked structures with the lowest non-bond energies. Molecular dynamics was used to generate the docked structures, followed by molecular mechanics to local minima on the CDB–DEH potential surface. The electrostatic energy contribution to the non-bond interaction energy between DEH and CDB was evaluated using the Biosym CVFF force field using the CVFF partial charges. The partial atomic charges are summarized in Table 1. Minimization of the docked DEH–CDB structures were allowed to proceed freely, i.e., no intermolecular constraints were imposed. A starting structure was determined by manually docking DEH onto CDB while interactively monitoring the nonbond energy. A starting structure very similar to that shown in Figure 9 was used. After 1000 docked structures were generated by the molecular dynamics and mechanics steps, the structures were evaluated and two additional starting structures were produced and used for ≈700 molecular dynamics runs each. The second starting structure was similar to that shown in Figure 13 where the DEH and CDB π planes were perpendicular. The third starting structure was a coplanar side-by-side.

Table 1. CVFF Partial Atomic Charges for DEH and CDB (See Figure 2 for Atom Numbering Scheme)

atom	charge	atom	charge	atom	charge
		DEH			
N1	−0.550	N2	−0.300	N3	−0.220
C1	−0.300	C2	0.020	C3	0.020
C4	−0.300	C5	0.110	C6	−0.100
C7	−0.100	C8	0.000	C9	−0.100
C10	−0.100	C11	0.200	C12	0.110
C13	−0.100	C14	−0.100	C15	−0.100
C16	−0.100	C17	−0.100	C18	0.110
C19	−0.100	C20	−0.100	C21	−0.100
C22	−0.100	C23	−0.100	H(C1)	0.100
H(C1)	0.100	H(C1)	0.100	H(C2)	0.100
H(C2)	0.100	H(C3)	0.100	H(C3)	0.100
H(C4)	0.100	H(C4)	0.100	H(C4)	0.100
H(C6)	0.100	H(C7)	0.100	H(C9)	0.100
H(C10)	0.100	H(C11)	0.100	H(C13)	0.100
H(C14)	0.100	H(C15)	0.100	H(C16)	0.100
H(C17)	0.100	H(C19)	0.100	H(C20)	0.100
H(C21)	0.100	H(C22)	0.100	H(C23)	0.100
		CDB			
N1	−0.390	N2	−0.199	N3	−0.390
O1	−0.380	O2	−0.380	C1	−0.102
C1	0.110	C2	0.102	C3	−0.100
C4	0.000	C5	−0.100	C6	−0.100
C7	0.379	C8	0.022	C9	0.358
C10	−0.100	C11	0.000	C12	−0.100
C13	−0.100	C14	−0.100	C15	−0.100
C16	0.000	C17	0.201	C18	0.110
C19	−0.100	C20	−0.100	C21	−0.100
C22	−0.100	C23	−0.100	H(N1)	0.280
H(N3)	0.280	H(C3)	0.100	H(C5)	0.100
H(C6)	0.100	H(C10)	0.100	H(C12)	0.100
H(C13)	0.100	H(C14)	0.100	H(C15)	0.100
H(C19)	0.100	H(C20)	0.100	H(C21)	0.100
H(C22)	0.100	H(C23)	0.100		

The dynamics runs were conducted at 900 K for 1200 ps (time step of 1 fs) in order to adequately sample the potential energy surface. The docked structures were saved every 0.5 ps during the computer simulation. The resulting 2370 dynamic structures were minimized (gradient 0.001 kcal/mol) and subsequently examined. All computations were performed on IBM RISC 6000 Model 530, 540, and 560 computers.

Results and Discussion

The population of docked CDB–DEH structures as a function of total energy (eq 1) is presented in Figure 3. These are docked structures that have been generated at 900 K then minimized at 0 K. Of the 2370 docked structures generated, 351 are unique both in energy and structure. The most probable distribution of conformers at temperature T is given by[9]

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[8] Pacansky, J.; Waltman, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5813.

[9] Reif, F. *Fundamentals of Statistical and Thermal Physics*; McGraw-Hill Book Co.: New York, 1065; p 204.

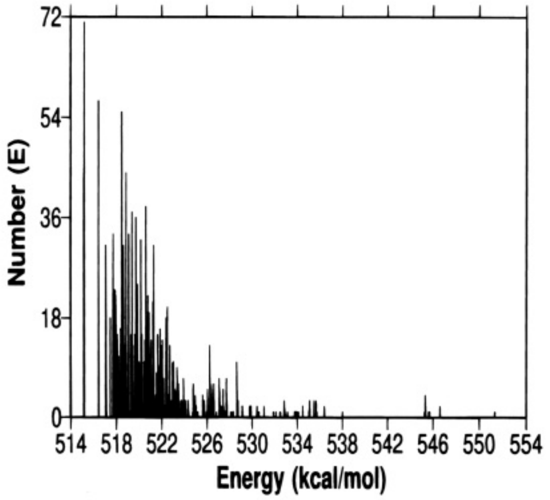

Figure 3. Population versus total energy (see eq 1) of DEH-CDB docked structures.

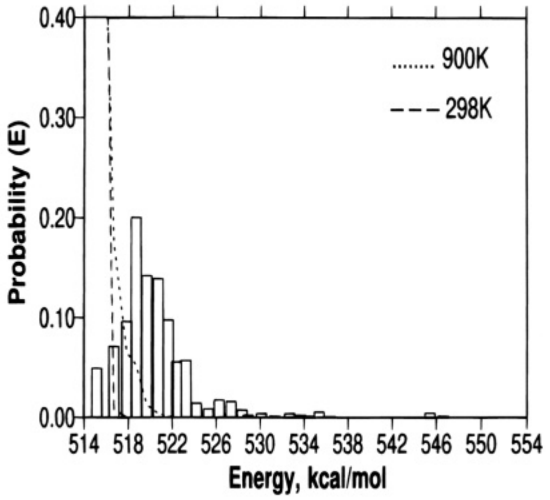

Figure 4. Probability distribution of DEH−CDB docked structures. The energy axis is total energy defined in eq 1. The bar graph indicates the fraction of docked structures occupying an energy bin of energy width 1.00*kT*. The two dashed lines indicate the most probable distribution of docked structures at the molecular dynamics temperature of 900 K (short dash) and at 298 K (long dash).

$$P_\beta(E_i) = n(E_i)e^{-\beta E_i}/\sum n(E_i)e^{-\beta E_i} \qquad (3)$$

where $\beta = 1/kT$, $P_\beta(E_i)$ is the probability at temperature *T*, and $n(E_i)$ is the number of conformers with energy E_i. Since the molecular dynamics computations were performed at 900 K, the results in Figure 4 provide the most probable distribution at 900 K. To extrapolate the data to room temperature or any other temperature, the most probable distribution at any temperature *T*′ is given by

$$P_{\beta'}(E_i) = P_\beta(E_i)e^{(\beta-\beta')E_i}\sum n(E_i)e^{-\beta E_i}/\sum n(E_i)e^{-\beta' E_i} \qquad (4)$$

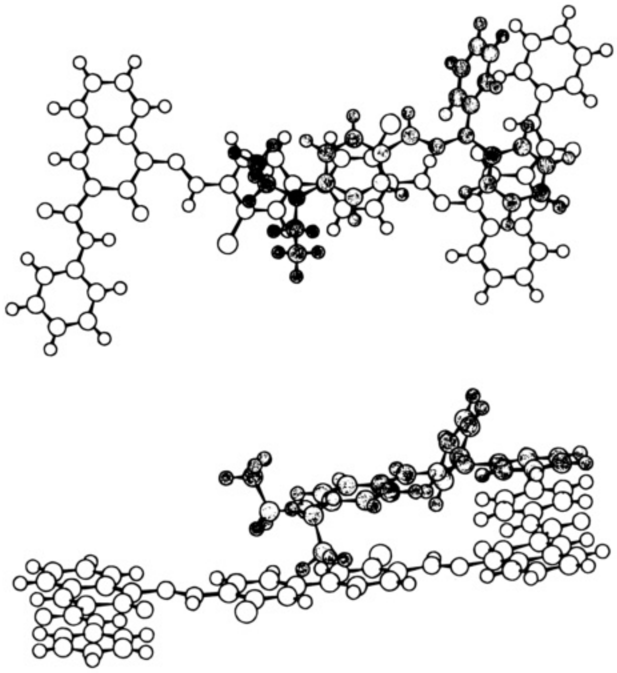

Figure 5. Docked DEH−CDB structure with the lowest non-bond interaction energy $E_{\text{inter}} = -40.9441$ kcal/mol, or $\Delta E_{\text{inter}} = 0.0$ kcal/mol. The shaded atoms represent the DEH molecule. In the top perspective, DEH is situated above the CDB molecule.

Table 2. Bin Average Total Energy (Eq 1) and Probability

bin	*E* (kcal/mol)	$P_{298\text{K}}$	$P_{900\text{K}}$
1	515.2	0.992	0.687
2	516.7	0.008	0.177
3	517.9	0.000	0.065
4	518.7	0.000	0.053
5	519.7	0.000	0.013
6	520.7	0.000	0.004
7	521.6	0.000	0.001

where $\beta' = 1/kT'$, and $P_{\beta'}(E_i)$ is the probability at temperature *T*′. The most probable distributions of docked CDB−DEH structures at 900 and 298 K as a function of energy (eq 1) are presented in Figure 4. The energy axis has been grouped into energy "bins" having "bin widths" in multiples of 1.0*kT*. This conveniently groups docked structures of similar energy together, thereby facilitating interpretation of results. At a bin width of 1*kT*, there is a 99% probability at room temperature that the DEH−CDB docked structure can be found within the first energy bin (Table 2). The docked structures found in energy bin 2 are higher in energy by 1.3 kcal/mol or more and have a 1% probability of occurrence. Of the 117 total docked structures that populate energy bin 1, only two are unique. Moreover, only 0.035 kcal/mol in total energy separate the two structures. Both docked structures are nearly identical, with very minor differences in structural parameters, i.e., inter- and intramolecular bonding. Since the lowest energy docked structure is representative of both, it is presented in Figure 5. The Cartesian coordinates are summarized in Table 3. This docked structure also has the smallest non-bond or intermolecular interaction energy, $E_{\text{inter}} = -40.94$ kcal/mol, and hereafter is considered to be the global minimum among the 351 unique docked structures generated here, i.e., $\Delta E_{\text{inter}} = 0.0$ kcal/mol. In this docked structure, the π plane of DEH sits approximately 4 Å above the π plane of CDB. We observe that the diphenylhydrazone amine fragment in DEH interacts strongly with both the hydrazone−quinone and amido groups in CDB. The CVFF partial charges listed in Table 1 identify the heteroatoms on these groups as having relatively large partial atomic charges. For example, the large partial negative charges on the amido nitrogen and oxygen atoms on CDB attract the positive hydrogen atoms on

Table 3. Cartesian Coordinates (Å) of the Lowest Energy Docked Structure Shown in Figure 5

atom	*X*	*Y*	*Z*	atom	*X*	*Y*	*Z*
C	8.794 199 944	−5.222 022 533	−16.263 431 549	N	16.923 656 464	−3.454 023 600	−3.498 399 496
C	8.178 155 899	−5.530 404 568	−15.065 958 977	H	17.875 747 681	−3.174 823 761	−3.782 078 743
C	9.034 316 063	−5.499 909 878	−13.795 823 097	O	19.395 519 257	−2.638 990 402	−2.302 266 121
C	10.490 283 012	−5.028 615 475	−13.938 635 826	C	21.143 110 275	−2.008 474 112	0.079 220 437
C	10.970 061 302	−4.702 261 925	−15.221 319 199	O	21.744 358 063	−1.781 510 830	1.132 886 052
C	10.113 310 814	−4.820 774 555	−16.368 864 059	N	21.775 774 002	−1.857 300 639	−1.101 292 372
C	12.289 610 863	−4.238 662 720	−15.437 819 481	H	21.163 061 142	−2.078 638 077	−1.898 918 033
H	12.988 604 546	−4.117 749 214	−14.620 509 148	C	24.650 411 606	−1.052 042 365	−3.338 459 730
C	12.741 914 749	−3.912 387 133	−16.707 405 090	C	25.646 932 602	−0.708 445 549	−2.429 538 965
H	13.753 913 879	−3.557 571 650	−16.844 568 253	C	25.385 915 756	−0.737 044 871	−1.062 741 637
C	11.902 259 827	−4.038 630 009	−17.800 292 969	C	24.124 643 326	−1.110 292 315	−0.602 515 340
H	12.263 121 605	−3.780 425 549	−18.786 119 461	C	23.111 965 179	−1.458 692 074	−1.509 541 869
C	10.601 525 307	−4.489 305 973	−17.638 809 204	C	23.388 570 786	−1.425 468 802	−2.879 352 808
H	9.977 086 067	−4.561 753 273	−18.520 656 586	H	24.855 541 229	−1.029 380 083	−4.399 367 809
H	8.188 864 708	−5.257 544 041	−17.162 237 167	H	26.625 474 930	−0.419 017 702	−2.785 325 289
C	11.437 145 233	−5.171 075 821	−9.028 023 720	H	26.160 350 800	−0.470 252 842	−0.357 678 562
C	12.255 950 928	−4.968 500 137	−7.923 269 272	H	23.950 819 016	−1.123 598 814	0.462 135 971
C	13.608 292 580	−4.546 662 807	−8.041 803 360	H	22.628 250 122	−1.689 071 655	−3.601 611 614
C	14.065 069 199	−4.333 441 734	−9.369 863 510	C	11.248 035 431	−1.433 881 760	−8.418 767 929
C	13.247 469 902	−4.522 592 068	−10.474 456 787	C	12.464 499 474	−1.084 740 758	−7.841 683 865
C	11.929 105 759	−4.948 796 272	−10.314 431 190	C	13.555 394 173	−0.680 234 075	−8.629 466 057
Cl	9.761 987 686	−5.670 483 112	−8.751 440 048	C	13.377 398 491	−0.645 135 164	−10.023 449 898
H	11.782 680 511	−5.156 161 785	−6.974 991 798	C	12.159 980 774	−0.986 188 769	−10.603 771 210
H	15.053 722 382	−3.973 351 002	−9.600 360 870	C	11.081 219 673	−1.388 296 604	−9.804 515 839
H	13.641 318 321	−4.317 916 393	−11.459 794 998	H	10.436 530 113	−1.736 563 444	−7.771 230 698
N	11.318 273 544	−4.888 610 840	−12.773 777 008	H	12.539 682 388	−1.128 240 585	−6.767 380 238
N	11.039 827 347	−5.110 359 669	−11.451 669 693	H	14.181 453 705	−0.357 800 633	−10.680 988 312
H	10.093 769 073	−5.418 989 182	−11.182 680 130	H	12.060 412 407	−0.944 953 918	−11.679 652 214
O	8.559 989 929	−5.845 786 572	−12.704 501 152	N	14.863 005 638	−0.291 383 743	−8.002 779 007
C	6.681 699 276	−5.843 646 049	−15.072 067 261	C	16.022 756 577	0.220 014 364	−8.791 724 205
O	6.035 600 185	−5.843 791 962	−16.124 040 604	H	16.661 497 116	0.890 168 190	−8.181 684 494
N	6.064 292 908	−6.110 921 860	−13.904 995 918	H	15.679 890 633	0.874 333 203	−9.616 008 759
H	6.714 910 984	−6.071 400 642	−13.107 435 226	C	15.113 203 049	−0.351 198 018	−6.531 700 134
C	3.178 349 972	−6.991 266 251	−11.712 985 992	H	16.187 700 272	−0.516 236 365	−6.313 564 777
C	2.131 260 395	−7.088 595 390	−12.624 637 604	H	14.624 043 465	−1.236 492 872	−6.082 939 148
C	2.362 578 154	−6.871 829 510	−13.979 956 627	C	9.703 285 217	−1.742 685 795	−10.377 362 251
C	3.644 214 869	−6.553 254 128	−14.425 025 940	H	8.928 152 084	−2.035 955 667	−9.669 195 175
C	4.705 287 933	−6.441 038 609	−13.513 496 399	N	9.412 384 987	−1.704 010 129	−11.623 176 575
C	4.459 980 965	−6.674 331 665	−12.158 171 654	N	8.265 489 578	−2.031 910 896	−12.379 324 913
H	2.998 564 482	−7.165 091 515	−10.661 686 897	C	14.637 464 523	0.931 760 788	−5.839 095 116
H	1.137 227 178	−7.336 071 014	−12.280 545 235	H	15.166 309 357	1.821 996 450	−6.225 471 497
H	1.549 858 928	−6.950 925 827	−14.687 878 609	H	13.556 192 398	1.100 986 600	−5.994 761 467
H	3.794 224 262	−6.389 424 801	−15.480 630 875	H	14.812 541 962	0.888 769 329	−4.749 418 259
H	5.262 564 659	−6.614 050 865	−11.437 277 794	C	16.868 217 468	−0.938 731 909	−9.335 102 081
C	19.040 559 769	−2.612 994 671	1.302 243 233	H	17.297 231 674	−1.542 833 805	−8.515 635 490
C	19.681 861 877	−2.461 025 953	0.087 688 640	H	16.269 691 467	−1.619 788 647	−9.967 442 513
C	18.877 008 438	−2.758 756 876	−1.183 020 115	H	17.709 857 941	−0.570 592 761	−9.948 131 561
C	17.415 342 331	−3.204 956 055	−1.009 037 256	C	8.443 408 012	−1.504 172 325	−16.684 059 143
C	16.897 472 382	−3.314 894 915	0.295 671 910	C	9.540 108 681	−1.168 165 803	−15.902 363 777
C	17.723 323 822	−3.015 415 430	1.433 616 757	C	9.483 103 752	−1.334 850 430	−14.522 509 575
C	15.563 897 133	−3.717 943 430	0.545 499 444	C	8.323 664 665	−1.833 194 494	−13.884 933 472
H	14.883 741 379	−3.960 011 005	−0.260 876 983	C	7.239 406 586	−2.186 095 476	−14.716 982 841
C	15.069 811 821	−3.820 867 777	1.837 225 080	C	7.294 013 023	−2.014 370 680	−16.096 427 917
H	14.047 014 236	−4.131 339 550	2.000 714 302	H	8.489 833 832	−1.380 838 633	−17.756 565 094
C	15.881 284 714	−3.527 913 332	2.919 392 109	H	10.439 155 579	−0.786 298 215	−16.364 795 685
H	15.487 183 571	−3.611 254 454	3.922 842 264	H	10.357 043 266	−1.067 346 931	−13.947 540 283
C	17.194 646 835	−3.129 057 884	2.725 550 175	H	6.341 902 256	−2.628 037 214	−14.313 213 348
H	17.791 772 842	−2.910 557 985	3.602 532 625	H	6.450 043 678	−2.298 375 368	−16.709 693 909
H	19.611 591 339	−2.401 881 933	2.199 924 231	C	4.743 123 055	−3.409 013 271	−10.335 726 738
C	16.593 139 648	−3.640 462 399	−5.925 494 194	C	5.944 563 866	−4.093 962 193	−10.184 659 004
C	15.789 372 444	−3.899 908 781	−7.028 796 673	C	7.080 718 994	−3.658 207 655	−10.859 353 065
C	14.427 655 220	−4.288 445 473	−6.908 185 005	C	7.035 297 394	−2.522 383 928	−11.683 099 747
C	13.951 429 367	−4.431 671 143	−5.577 350 140	C	5.818 278 790	−1.835 477 233	−11.810 788 155
C	14.748 384 476	−4.165 320 396	−4.471 857 071	C	4.677 359 581	−2.281 239 033	−11.147 972 107
C	16.073 312 759	−3.761 498 690	−4.636 450 291	H	3.857 116 938	−3.756 145 954	−9.823 578 835
Cl	18.268 684 387	−3.143 133 879	−6.203 436 375	H	5.993 751 526	−4.970 928 669	−9.555 108 070
H	16.280 033 112	−3.778 017 044	−7.978 976 727	H	8.004 965 782	−4.206 170 082	−10.747 848 511
H	12.942 990 303	−4.730 480 671	−5.344 281 673	H	5.761 081 696	−0.974 032 809	−12.423 377 037
H	14.327 775 002	−4.272 531 986	−3.481 922 626	H	3.743 525 982	−1.749 101 996	−11.260 773 659
N	16.609 718 323	−3.499 421 120	−2.164 285 421				

a benzene ring of the DEH diphenylhydrazone moiety. The negatively charged imine and amine nitrogen atoms of the DEH diphenyl hydrazone group attracts the relatively positive hydrogen atoms on the CDB hydrazone–quinone and amido groups. The relevant close contact distances that arise as a result are summarized in Figure 6. A close contact intermolecular distance of 3.6 Å is observed between the electron-rich amido oxygen on CDB and the two hydrogen atoms of the DEH diphenylhydrazone group. The negatively charged imi-

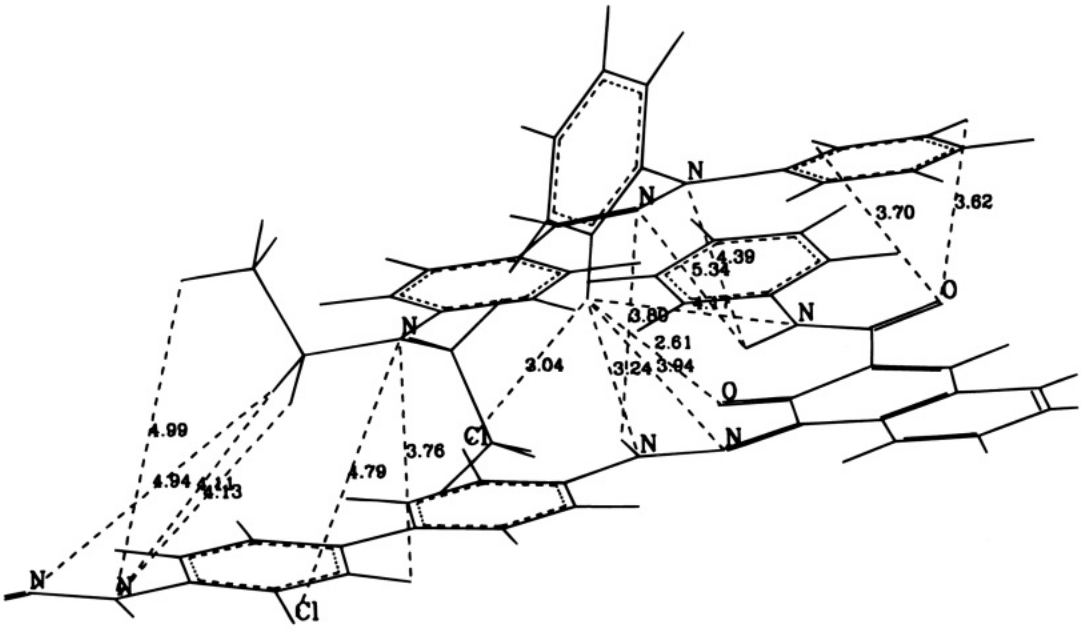

Figure 6. Close contacts identified in the docked DEH−CDB complex, $\Delta E_{\text{inter}} = 0.0$ kcal/mol.

ne and amine nitrogen atoms of the DEH diphenylhydrazone are within 3.8−5.3 Å of the hydrogen atoms on the CDB hydrazone−quinone and amido groups. A perpendicular phenyl ring hydrogen atom of the DEH diphenylhydrazone group also shows a very close contact of 2.6 Å with the electron-deficient CDB hydrazone−quinone carbonyl oxygen atom. This is the shortest intermolecular distance encountered between the two molecules and is consistent with hydrogen-bonding distances. Close contact distances of ≈4.1 Å are additionally obtained for other DEH diethylaniline ethyl hydrogen atoms and the CDB hydrazone−quinone nitrogen atoms (Figure 6). The DEH diethylaniline nitrogen atom has a close contact distance of 3.8 Å with a positively charged CDB chlorobiphenyl hydrogen atom. These are some of the close contact interactions that provide the “locking” features of DEH onto CDB.

The fact that the DEH diphenylhydrazone group is docked relatively close to the CDB amido group has a rather significant consequence. Experimentally, it is known that the phenylamido group is responsible for imparting a long-wavelength shift in the optical absorption of CDB necessary for photoconduction.[8] A 3-21G orbital plot for the highest occupied molecular orbital (HOMO) also reveals that the phenylamido group contributes strongly to the HOMO.[8] In DEH, both experimental and theoretical studies have shown that the most likely ionization sites occur on the aniline amine and hydrazone amine nitrogen atoms.[10−12] These data imply strong coupling between these structural moieties in CDB and DEH which may play a major role in carrier injection and photochemically induced electrical fatigue, since the results of the molecular docking studies presented here also place significance on these interactions.

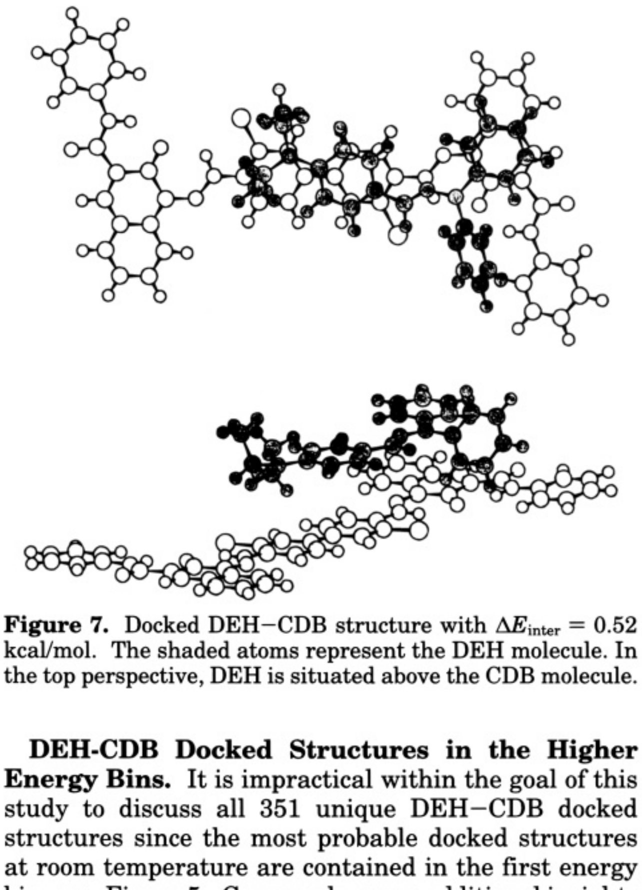

Figure 7. Docked DEH−CDB structure with $\Delta E_{\text{inter}} = 0.52$ kcal/mol. The shaded atoms represent the DEH molecule. In the top perspective, DEH is situated above the CDB molecule.

DEH-CDB Docked Structures in the Higher Energy Bins. It is impractical within the goal of this study to discuss all 351 unique DEH−CDB docked structures since the most probable docked structures at room temperature are contained in the first energy bin, e.g., Figure 5. Conversely, some additional insights may be gathered by investigating some of the other DEH−CDB docked structures that occur in the higher energy bins and that have larger nonbond interaction energies. Some examples of these kinds of docked structures are illustrated in Figures 7−15. In energy bin 2, a docked structure that is frequently encountered is one whereby the DEH diethylamine ethyl groups are cis instead of the more favourable trans[7] and directed away from the CDB π plane (Figure 7). The ΔE_{inter} is 0.52 kcal/mol. In this docked structure, the spatial

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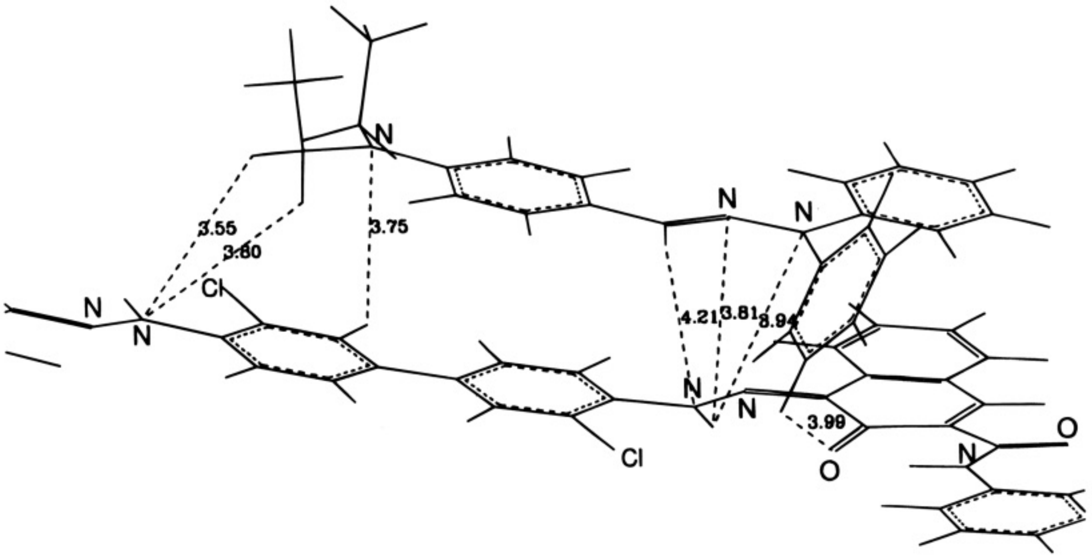

Figure 8. Close contacts identified in the docked DEH−CDB complex, $\Delta E_{\text{inter}} = 0.52$ kcal/mol.

orientation of the DEH molecule relative to CDB is very similar to the $\Delta E_{\text{inter}} = 0.0$ kcal/mol docked structure (Figure 5); however, with both of the DEH ethyl groups being cis (instead of trans) and spatially directed away from the CDB π plane, the DEH π plane sits only ≈3.8 Å above the CDB π plane. The locking features in this molecule involve close contacts between the DEH diphenylhydrazone groups with the CDB amido and hydrazone−quinone, and between the DEH diethylaniline and the CDB hydrazone−quinone groups (Figure 8).

Docked structures with the DEH diethyl group cis and spatially directed toward CDB were also encountered; however, these were generally higher in both total and non-bond energy and typically occurred in energy bin 5 and higher. An example of one such structure is presented in Figure 9. In this docked structure, the π plane of DEH sits ≈4 Å above the π plane of CDB. To avoid steric repulsion between the downward directed DEH ethyl groups and CDB, the DEH molecule partially translates away from CDB so that the ethyl groups are well away from CDB and the two π planes may be within ≈4 Å. The locking features are primarily limited to the DEH diphenylhydrazone group with the CDB amido and hydrazone−quinone groups (Figure 10). ΔE_{inter} for this docked structure is 5 kcal/mol.

In Figure 11, a low-energy docked structure from energy bin 3 is presented. Here the DEH diethylaniline group, instead of the diphenylhydrazone group, interacts with the CDB amido group. The DEH diphenylhydrazone moiety instead interacts with the CDB hydrazone−quinone. The π plane of DEH sits ≈4 Å above the π plane of CDB. The nonbond interaction energy ΔE_{inter} is 2.45 kcal/mol relative to the lowest energy docked structure shown previously in Figure 5. The locking features in this docked structure are summarized in Figure 12. Distances of ≈2.7−4.1 Å are observed between the positive hydrogen atoms of the diethylaniline ethyl groups and the electron-rich CDB amido oxygen and nitrogen atoms.

Figure 13 shows another docked structure whereby the DEH molecule is oriented somewhat orthogonally to the CDB π plane. This docked structure was found in energy bin 20 and is an extremely low probability conformation even at 900 K; ΔE_{inter} is 19.9 kcal/mol. Figure 14 summarizes some of the close contact distances between the two molecules.

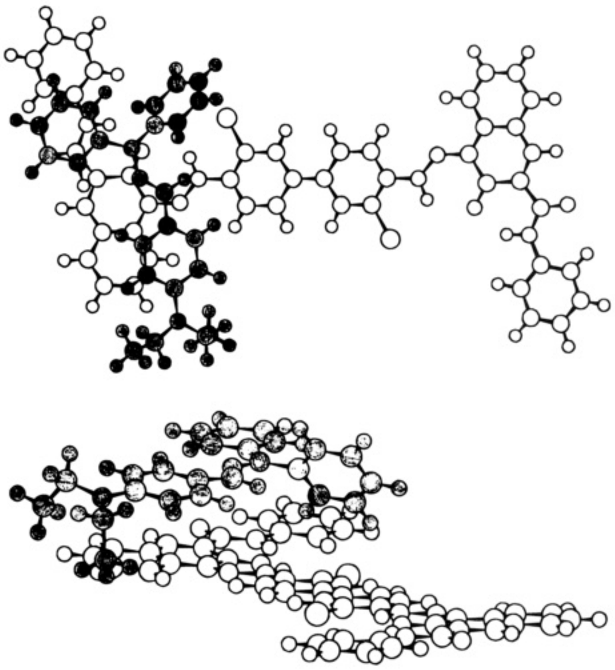

Figure 9. Docked DEH−CDB structure with $\Delta E_{\text{inter}} = 5.21$ kcal/mol. The shaded atoms represent the DEH molecule. In the top perspective, DEH is situated above the CDB molecule.

Inspection of the docked DEH−CDB structures in all of the energy bins allow several conclusions to be made about the preferred docking and interaction between DEH and CDB. (1) The docked structures with the lowest non-bond interaction energies invariably are positioned such that the DEH diphenylhydrazone structural moiety lies over the CDB amido and hydrazone−quinone groups, e.g., Figure 5; all unique docked structures within the first two energy bins have these interactions. (2) Docked structures where the DEH diethylaniline group is positioned over the CDB amido and hydrazone−quinone are ≈2 kcal/mol higher in non-

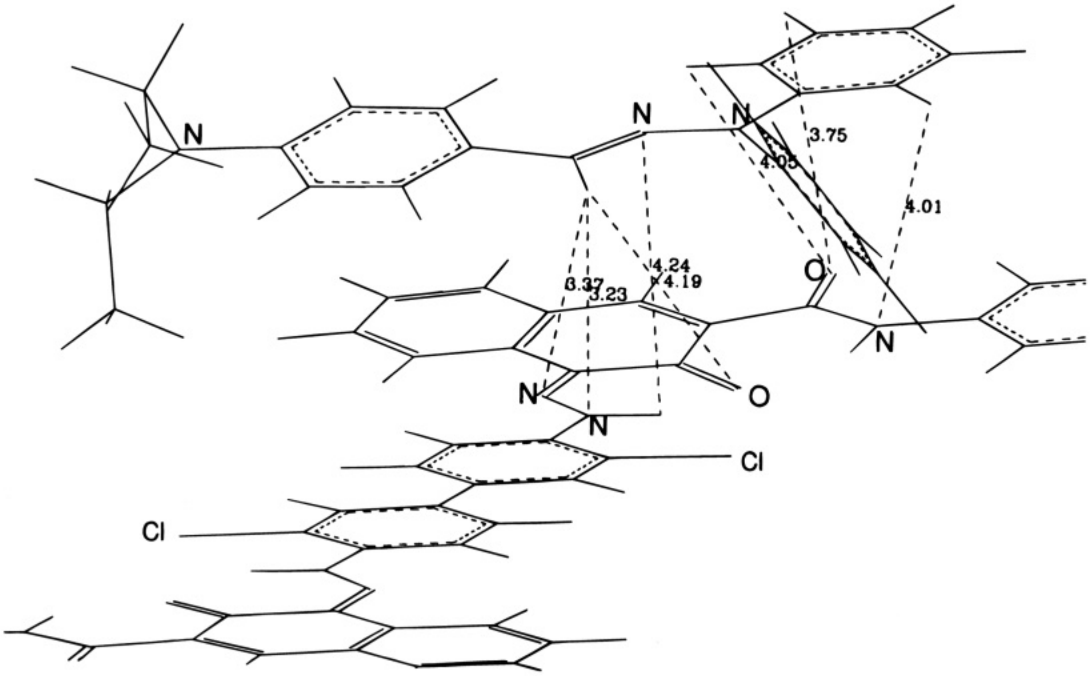

Figure 10. Close contacts identified in the docked DEH−CDB complex, $\Delta E_{\text{inter}} = 5.21$ kcal/mol.

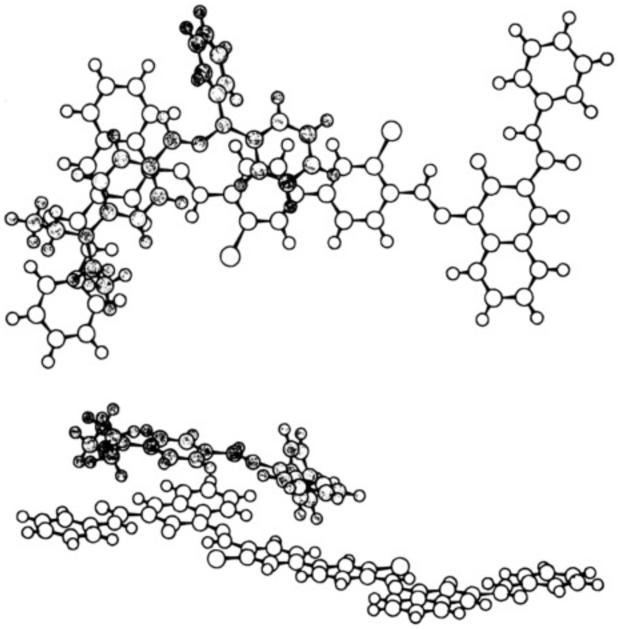

Figure 11. Docked DEH−CDB structure with $\Delta E_{\text{inter}} = 2.45$ kcal/mol. The shaded atoms represent the DEH molecule. In the top perspective, DEH is situated above the CDB molecule.

bond interaction energy and these docked structures occur in energy bins 3 and higher. (3) Docked structures whereby both the diphenylhydrazone and diethylaniline groups on DEH interact with CDB are lower in nonbond interaction energy compared to when only one of the two DEH groups interacts with CDB; see, for example, Figure 11. (4) Perpendicular or near perpendicular orientations of DEH to CDB are high-energy structures with low probability of occurrence.

Validity of the Molecular Dynamics Simulation. While the majority of the low-energy docked DEH−CDB structures encountered exhibit strong intermolecular interactions between either the diphenylhydrazone portion of DEH with the phenylamido and hydrazone−quinone structural moieties in CDB, as discussed above, or between the diethylaniline portion of DEH with the phenylamido and hydrazone−quinone structural moieties in CDB, many other local minima were also computed giving rise to multiple minima. Since there exists no general solution to the multiple minimum problem,[13] care must be exercised to examine a variety of starting docked structures to have reasonable statistical certainty that the global minimum has been found. By generating a total of 2370 conformers at a relatively high dynamics temperature of 900 K, from three considerably different starting docked structures, we hope to have sampled enough of the complex multidimensional potential surface here to have considered many of the intermolecular interactions possible between DEH and CDB. An attempt to establish the validity of the computer simulation is presented in Figure 15. Since the most probable distribution falls exponentially (eq 3), one indication for the validity of the simulation may be established by comparing the most probable distribution curve obtained from the molecular dynamics run at 900 K (Figure 4) with an exponential decay that would be expected at 900 K, i.e., $e^{-E/kT}$, where $T = 900$ K. These two curves should coincide when good molecular dynamics statistics have been generated. The slopes of these lines ($1/kT$) on a semilogarithmic plot are presented in Figure 15. The solid circles are data points obtained from the molecular dynamics simulation, and the slope is obtained from a least-squares fit of the data points. Coincidence is obtained for a computed exponential decay of 820 K, which is close to the molecular dynamics temperature of 900 K.

Concluding Remarks

DEH and CDB are important organic molecules used in photoconductor technology. While cost performance still favors their widespread use, organic photoconductors today still suffer from comparatively shorter life-

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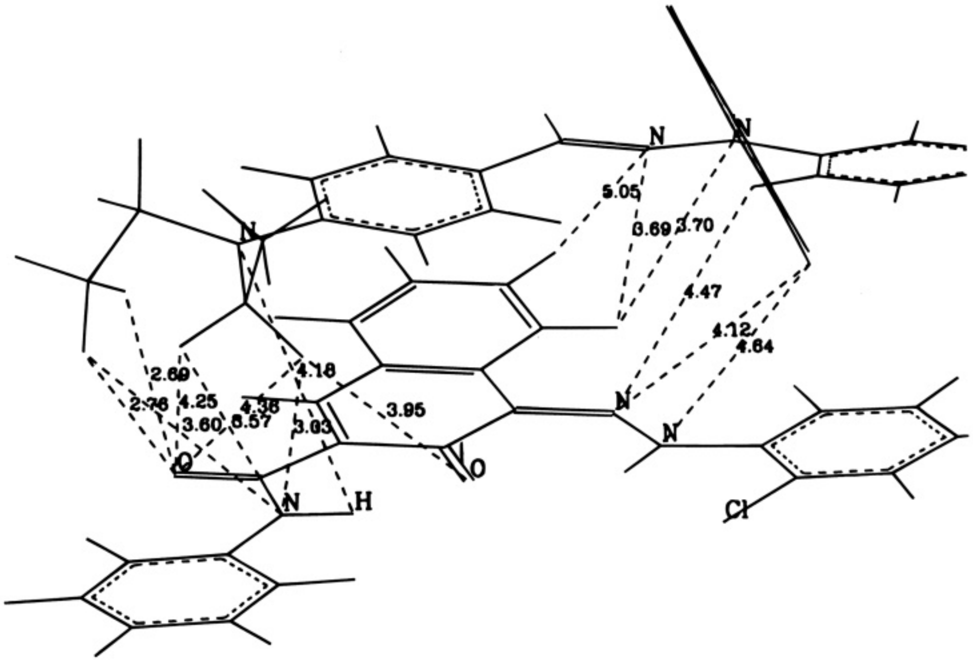

Figure 12. Close contacts identified in the docked DEH–CDB complex, $\Delta E_{\text{inter}} = 2.45$ kcal/mol.

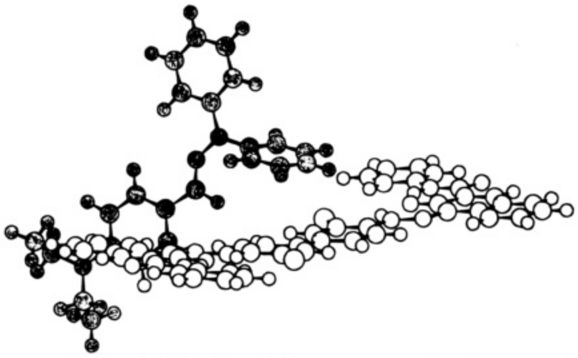

Figure 13. Docked DEH–CDB structure with $\Delta E_{\text{inter}} = 19.92$ kcal/mol. The shaded atoms represent the DEH molecule.

times than chalcogenide- or silicon-based photoconductors. To provide more robust photoconductors, electrical fatigue due to photochemistry of the organic components must be minimized or eliminated. To provide faster photoconductors, carrier injection efficiencies must be increased. Both of these processes occur at the interface between the carrier generation and transport layers, consequently, a better understanding of this interface is required. Molecular docking studies were therefore performed on DEH and CDB. The results of the molecular dynamics docking studies favor a strong interaction between either the diphenylhydrazone or the diethylaniline structural moiety in DEH with the phenyl

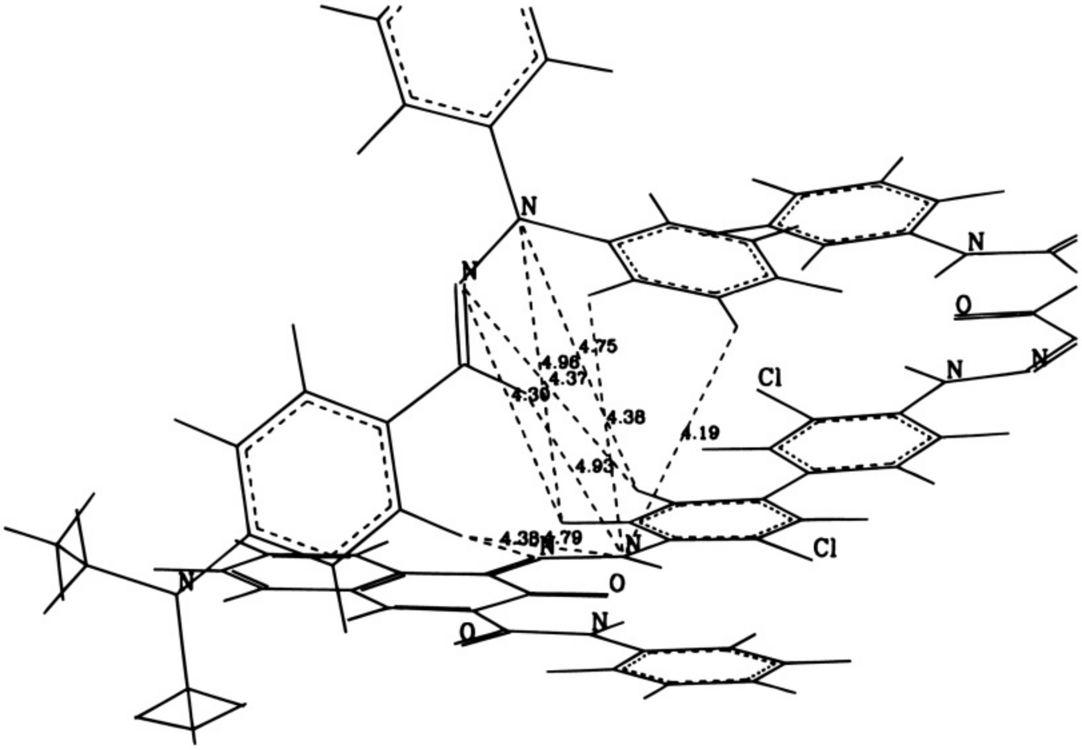

Figure 14. Close contacts identified in the docked DEH–CDB complex, $\Delta E_{\text{inter}} = 19.92$ kcal/mol.

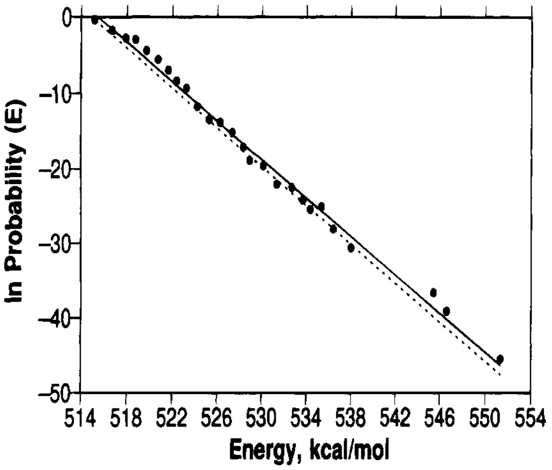

Figure 15. Probability versus total energy (eq 1). The data points (●) represent the actual molecular dynamics data, and the solid line is a least-squares fit of the data points. The dashed line is the expected decay at 820 K. These two lines have the same slope.

amido group in CDB and implicates these intermolecular interactions as the important ones in photoconduction and photochemistry. The results of the docking studies are consistent with experimental and theoretical data. For example, ionization (i.e., hole injection) of DEH initially occurs on the aniline amine or hydrazone amine nitrogen atom.[11,14,15] The results of the docking studies presented here indicate that the low-energy docked structures exhibit close contacts between the DEH amine nitrogen atoms and CDB.

Docking studies are also beneficial from the standpoint of the identification of the important intermolecular interaction sites. This provides a direction for chemical modification of molecules such as DEH and CDB to improve, for example, photoconductive properties or increase resistance to photochemistry while simultaneously preserving the important interactions necessary for photoconduction.

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