**Supplementary material.**

Experimental and database transferred electron density analysis and evaluation of electrostatic forces in coumarin-102 dye

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**Table S1:** Topological properties at the bond critical points of intramolecular covalent bonds in coumarin-102 for the EXPLM experimental multipolar model (first entry) and ELMAM2 model (second entry in italics).

| Bond | $d_{A1-A2}$ | $d_{A1-CP}$ | $d_{CP-A2}$ | $\rho_{cp}$ | $\nabla^2\rho_{cp}$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\varepsilon$ |
|---|---|---|---|---|---|---|---|---|---|
| | | (Å) | | (e/Å$^3$) | (e/Å5) | (e/Å$^5$) | | | |
| O11— C2 | 1.2211 | 0.7818 | 0.4393 | 2.9634 | -33.89 | -29.33 | -25.76 | 21.19 | 0.14 |
| | *1.2211* | *0.7970* | *0.4241* | *3.0505* | *-32.75* | *-30.45* | *-26.15* | *23.85* | *0.16* |
| O1—C2 | 1.3776 | 0.8265 | 0.5519 | 1.9458 | -14.28 | -15.50 | -14.32 | 15.54 | 0.08 |
| | *1.3773* | *0.8399* | *0.5387* | *1.9855* | *-17.03* | *-15.66* | *-13.98* | *12.61* | *0.12* |
| O1— C9 | 1.3768 | 0.8276 | 0.5498 | 1.9171 | -13.36 | -15.28 | -13.60 | 15.52 | 0.12 |
| | *1.3784* | *0.8309* | *0.5476* | *1.9411* | *-13.94* | *-15.24* | *-13.28* | *14.58* | *0.15* |
| C2—C3 | 1.4434 | 0.7470 | 0.6965 | 1.9689 | -15.68 | -15.24 | -12.52 | 12.07 | 0.22 |
| | *1.4442* | *0.7229* | *0.7213* | *2.0913* | *-18.42* | *-16.21* | *-12.98* | *10.77* | *0.25* |
| C3—C4 | 1.3692 | 0.6462 | 0.7230 | 2.2619 | -19.97 | -17.90 | -13.88 | 11.81 | 0.29 |
| | *1.3663* | *0.6796* | *0.6867* | *2.2322* | *-21.35* | *-17.29* | *-14.23* | *10.17* | *0.22* |
| C4—C10 | 1.4344 | 0.7227 | 0.7119 | 1.9428 | -14.84 | -14.52 | -12.51 | 12.19 | 0.16 |
| | *1.4363* | *0.7336* | *0.7026* | *1.9596* | *-15.04* | *-14.67* | *-12.05* | *11.68* | *0.22* |
| C5—C6 | 1.3785 | 0.6762 | 0.7024 | 2.1840 | -19.01 | -17.10 | -13.76 | 11.85 | 0.24 |
| | *1.3777* | *0.6979* | *0.6798* | *2.1474* | *-20.07* | *-16.45* | *-13.78* | *10.16* | *0.19* |
| C6—C7 | 1.4295 | 0.7124 | 0.717 | 2.0122 | -15.91 | -15.40 | -12.80 | 12.29 | 0.20 |
| | *1.4297* | *0.7226* | *0.7071* | *2.0184* | *-15.99* | *-15.35* | *-12.19* | *11.56* | *0.26* |
| C7—C8 | 1.4140 | 0.7155 | 0.6986 | 2.0492 | -16.57 | -15.93 | -12.84 | 12.19 | 0.24 |
| | *1.4143* | *0.7152* | *0.6992* | *1.9931* | *-15.72* | *-15.02* | *-12.01* | *11.31* | *0.25* |
| C8—C9 | 1.3903 | 0.6885 | 0.7019 | 2.1556 | -19.12 | -17.50 | -13.40 | 11.78 | 0.31 |
| | *1.3903* | *0.6769* | *0.7134* | *2.1172* | *-18.94* | *-16.60* | *-13.10* | *10.77* | *0.27* |
| C9—C10 | 1.4077 | 0.7302 | 0.6777 | 2.0850 | -17.19 | -16.11 | -13.02 | 11.93 | 0.24 |
| | *1.4061* | *0.7179* | *0.6882* | *2.0772* | *-17.72* | *-16.25* | *-12.65* | *11.18* | *0.28* |
| C5—C10 | 1.4126 | 0.7076 | 0.7051 | 2.0384 | -15.77 | -15.50 | -12.73 | 12.46 | 0.22 |
| | *1.4123* | *0.7175* | *0.6948* | *2.0172* | *-16.33* | *-15.08* | *-12.46* | *11.21* | *0.21* |
| C6—C12 | 1.5051 | 0.7752 | 0.7299 | 1.6912 | -10.04 | -11.62 | -10.79 | 12.37 | 0.08 |
| | *1.5061* | *0.7838* | *0.7223* | *1.7328* | *-10.90* | *-11.74* | *-10.61* | *11.44* | *0.11* |
| C12—C13 | 1.5269 | 0.7620 | 0.7651 | 1.6320 | -9.09 | -10.73 | -10.71 | 12.35 | 0.00 |
| | *1.5267* | *0.7635* | *0.7632* | *1.5965* | *-8.97* | *-9.94* | *-9.86* | *10.83* | *0.01* |
| C13—C14 | 1.5192 | 0.7519 | 0.7674 | 1.6483 | -9.30 | -11.09 | -10.83 | 12.62 | 0.02 |
| | *1.5182* | *0.7478* | *0.7704* | *1.6391* | *-9.62* | *-10.57* | *-10.22* | *11.18* | *0.03* |
| C8—C18 | 1.5066 | 0.7887 | 0.7179 | 1.6484 | -9.46 | -11.19 | -10.37 | 12.10 | 0.08 |
| | *1.5070* | *0.7705* | *0.7365* | *1.6733* | *-9.92* | *-11.28* | *-10.08* | *11.44* | *0.12* |
| C16—C17 | 1.5195 | 0.7895 | 0.7302 | 1.6631 | -9.33 | -11.18 | -10.92 | 12.77 | 0.02 |
| | *1.5192* | *0.7710* | *0.7483* | *1.6362* | *-9.58* | *-10.57* | *-10.19* | *11.18* | *0.04* |
| C17—C18 | 1.5273 | 0.7744 | 0.7529 | 1.5927 | -8.62 | -10.53 | -10.21 | 12.12 | 0.03 |
| | *1.5275* | *0.7637* | *0.7638* | *1.5934* | *-8.95* | *-9.93* | *-9.85* | *10.83* | *0.01* |
| C4—C23 | 1.4999 | 0.7806 | 0.7194 | 1.7013 | -10.23 | -11.78 | -10.85 | 12.40 | 0.09 |
| | *1.4997* | *0.7743* | *0.7254* | *1.6962* | *-10.36* | *-11.29* | *-10.35* | *11.28* | *0.09* |
| C7—N15 | 1.3710 | 0.5615 | 0.8095 | 2.1185 | -17.94 | -16.97 | -14.17 | 13.20 | 0.20 |
| | *1.3701* | *0.5534* | *0.8167* | *2.0784* | *-18.00* | *-16.12* | *-13.19* | *11.32* | *0.22* |
| C14—N15 | 1.4589 | 0.6429 | 0.8161 | 1.8010 | -9.78 | -13.74 | -12.07 | 16.02 | 0.14 |
| | *1.4592* | *0.6058* | *0.8536* | *1.7188* | *-9.87* | *-11.98* | *-10.68* | *12.79* | *0.12* |
| C16—N15 | 1.4572 | 0.6219 | 0.8354 | 1.7556 | -9.73 | -12.87 | -11.74 | 14.88 | 0.10 |
| | *1.4566* | *0.6035* | *0.8532* | *1.7261* | *-10.05* | *-12.03* | *-10.73* | *12.71* | *0.12* |

**Table S1:** continued.

| Bond | $d_{A1\text{-}A2}$ | $d_{A1\text{-}CP}$ | $d_{CP\text{-}A2}$ | $\rho_{cp}$ | $\nabla^2\rho_{cp}$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | ε |
|---|---|---|---|---|---|---|---|---|---|
| | | (Å) | | (e/Å$^3$) | (e/Å$^5$) | (e/Å$^5$) | | | |
| C3—H3 | 1.0830 | 0.6906 | 0.3924 | 1.9079 | -20.77 | -18.19 | -17.22 | 14.64 | 0.06 |
| | *1.0842* | *0.7104* | *0.3739* | *1.8730* | *-19.67* | *-17.97* | *-17.01* | *15.30* | *0.06* |
| C5—H5 | 1.0831 | 0.6858 | 0.3976 | 1.9089 | -20.88 | -18.05 | -17.11 | 14.28 | 0.05 |
| | *1.0795* | *0.7060* | *0.3735* | *1.8833* | *-20.09* | *-18.12* | *-17.14* | *15.17* | *0.06* |
| C12—H12A | 1.0871 | 0.6795 | 0.4080 | 1.8435 | -17.94 | -16.41 | -16.32 | 14.78 | 0.01 |
| | *1.0896* | *0.6903* | *0.3992* | *1.8119* | *-17.11* | *-15.82* | *-15.69* | *14.41* | *0.01* |
| C12—H12B | 1.0964 | 0.6993 | 0.3972 | 1.8043 | -16.63 | -16.18 | -15.91 | 15.46 | 0.02 |
| | 1.0921 | 0.6921 | 0.4000 | 1.8065 | -16.92 | -15.75 | -15.58 | 14.41 | 0.01 |
| C13—H13A | 1.0913 | 0.6838 | 0.4080 | 1.8510 | -18.42 | -16.60 | -16.56 | 14.75 | 0.00 |
| | *1.0909* | *0.6909* | *0.4000* | *1.8065* | *-17.03* | *-15.86* | *-15.56* | *14.38* | *0.02* |
| C13—H13B | 1.0929 | 0.7001 | 0.3928 | 1.8281 | -17.45 | -16.67 | -16.32 | 15.55 | 0.02 |
| | *1.0898* | *0.6902* | *0.3996* | *1.8104* | *-17.09* | *-15.84* | *-15.63* | *14.38* | *0.01* |
| C14—H14A | 1.0896 | 0.6736 | 0.4163 | 1.8122 | -18.29 | -16.16 | -16.08 | 13.96 | 0.00 |
| | *1.0955* | *0.7003* | *0.3952* | *1.8580* | *-18.37* | *-16.98* | *-16.38* | *14.99* | *0.04* |
| C14—H14B | 1.0942 | 0.7006 | 0.3936 | 1.8516 | -18.80 | -17.34 | -16.49 | 15.03 | 0.05 |
| | *1.0922* | *0.6982* | *0.3941* | *1.8670* | *-18.62* | *-17.07* | *-16.55* | *15.00* | *0.03* |
| C16—H16A | 1.0887 | 0.6808 | 0.4080 | 1.8400 | -18.57 | -16.85 | -16.11 | 14.40 | 0.05 |
| | *1.0944* | *0.6996* | *0.3948* | *1.8611* | *-18.44* | *-17.05* | *-16.38* | *15.00* | *0.04* |
| C16—H16B | 1.0952 | 0.6870 | 0.4083 | 1.8320 | -17.95 | -16.57 | -16.02 | 14.65 | 0.03 |
| | *1.0943* | *0.6996* | *0.3947* | *1.8613* | *-18.46* | *-17.00* | *-16.47* | *15.00* | *0.03* |
| C17—H17A | 1.0891 | 0.6804 | 0.4089 | 1.8137 | -17.44 | -16.04 | -16.02 | 14.62 | 0.00 |
| | *1.0890* | *0.6897* | *0.3993* | *1.8123* | *-17.16* | *-15.94* | *-15.60* | *14.38* | *0.02* |
| C17—H17B | 1.0946 | 0.7081 | 0.3865 | 1.8340 | -17.07 | -16.67 | -16.51 | 16.10 | 0.01 |
| | *1.0895* | *0.6901* | *0.3994* | *1.8117* | *-17.11* | *-15.77* | *-15.72* | *14.38* | *0.00* |
| C18—H18A | 1.0921 | 0.7134 | 0.3789 | 1.8486 | -18.86 | -17.33 | -17.27 | 15.74 | 0.00 |
| | *1.0890* | *0.6898* | *0.3992* | *1.8134* | *-17.16* | *-15.93* | *-15.62* | *14.39* | *0.02* |
| C18—H18B | 1.0921 | 0.7021 | 0.3900 | 1.8249 | -17.56 | -16.76 | -16.36 | 15.56 | 0.02 |
| | *1.0905* | *0.6909* | *0.3996* | *1.8104* | *-17.05* | *-15.85* | *-15.59* | *14.39* | *0.02* |
| C23—H23A | 1.0558 | 0.6950 | 0.3609 | 1.8983 | -19.21 | -17.93 | -17.67 | 16.38 | 0.01 |
| | *1.0587* | *0.6670* | *0.3918* | *1.8554* | *-17.51* | *-16.33* | *-15.53* | *14.34* | *0.05* |
| C23—H23B | 1.0609 | 0.6673 | 0.3938 | 1.8176 | -16.85 | -16.24 | -15.64 | 15.03 | 0.04 |
| | *1.0653* | *0.6718* | *0.3935* | *1.8389* | *-17.02* | *-16.07* | *-15.36* | *14.40* | *0.05* |
| C23—H23C | 1.0606 | 0.6727 | 0.3879 | 1.8040 | -16.66 | -16.19 | -15.62 | 15.15 | 0.04 |
| | *1.0626* | *0.6699* | *0.3927* | *1.8468* | *-17.24* | *-16.18* | *-15.43* | *14.38* | *0.05* |

$d_{A1\text{-}A2}$, $d_{A1\text{-}BCP}$ and $d_{BCP\text{-}A2}$ are respectively the distances between the two bonded atoms, between the first atom and the BCP, and between the BCP and the second atom. $\rho_{cp}$ is the total electron density at the CP. $\nabla^2\rho_{cp}$ its Laplacian. $\lambda_1$**,** $\lambda_2$**,** $\lambda_3$ are the eigenvalues of the Hessian matrix $\partial^2\rho/\partial x_i\partial x_j$. $\varepsilon = \lambda_1/\lambda_2 - 1$ is the ellipticity.

**Table S2:** Analysis of signal over noise ration $r=I/\sigma_I$ as a function of resolution for the C-102 diffraction data.

| S1 | S2 | #ref | <r> | r<=0 | 0<r<=1 | 1<r<=2 | 2<r<=3 | 3<r<=4 | 4<r<=6 | 6<r<=10 | r>10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.065 | 0.509 | 1374 | 84.939 | 0 | 38 | 26 | 20 | 16 | 26 | 29 | 1219 |
| 0.509 | 0.641 | 1348 | 61.946 | 0 | 96 | 65 | 26 | 18 | 29 | 58 | 1056 |
| 0.641 | 0.734 | 1377 | 49.703 | 0 | 96 | 121 | 18 | 27 | 38 | 64 | 1013 |
| 0.734 | 0.808 | 1354 | 38.714 | 0 | 123 | 122 | 37 | 40 | 44 | 79 | 909 |
| 0.808 | 0.870 | 1353 | 31.952 | 0 | 139 | 139 | 26 | 36 | 65 | 98 | 850 |
| 0.870 | 0.924 | 1354 | 23.748 | 0 | 157 | 198 | 49 | 41 | 76 | 100 | 733 |
| 0.924 | 0.973 | 1250 | 16.391 | 0 | 136 | 246 | 60 | 50 | 85 | 130 | 543 |
| 0.973 | 1.017 | 1231 | 12.011 | 0 | 157 | 280 | 84 | 66 | 85 | 124 | 435 |
| 1.017 | 1.058 | 1160 | 11.059 | 0 | 139 | 303 | 59 | 55 | 102 | 118 | 384 |
| 1.058 | 1.096 | 1000 | 10.878 | 0 | 125 | 294 | 55 | 48 | 71 | 101 | 306 |
| ..... | | | | | | | | | | | |
| All | | 12801 | 34.134 | 0 | 1206 | 1794 | 434 | 397 | 621 | 901 | 7448 |

**Table S3:** Covalent bond lengths and angles

| Bond lengths (Å) | | | |
|---|---|---|---|
| O1—C2 | 1.3776(4) | C7—N15 | 1.3710(3) |
| O1—C9 | 1.3768(4) | C14—N15 | 1.4589(4) |
| O11—C2 | 1.2211(5) | C16—N15 | 1.4572(4) |
| C2—C3 | 1.4434(4) | C12—C13 | 1.5269(4) |
| C3—C4 | 1.3692(4) | C13—C14 | 1.5192(4) |
| C4—C10 | 1.4344(4) | C4—C23 | 1.4999(4) |
| C5—C10 | 1.4126(4 ) | C16—C17 | 1.5195(4) |
| C5—C6 | 1.3785(3) | C17—C18 | 1.5273(4) |
| C6—C7 | 1.4295(3) | C6—C12 | 1.5051(3) |
| C7—C8 | 1.4140(3) | C8—C18 | 1.5066(3) |
| C8—C9 | 1.3903(3) | C9—C10 | 1.4077(3) |

| Bond angles | (°) | O1—C2—O11 | 116.40(4) |
|---|---|---|---|
| O1—C2—C3 | 117.38(3) | C7—N15—C16 | 122.32(3) |
| O1—C9—C8 | 115.98(2) | C7—N15—C14 | 122.85(2) |
| O1—C9—C10 | 120.64(3) | C14—N15—C16 | 114.69(3) |
| O11—C2—C3 | 126.22(4) | C8—C7—N15 | 120.35(2) |
| C2—O1—C9 | 122.27(3) | C13—C14—N15 | 112.20(3) |
| C2—C3—C4 | 121.79(3) | C6—C7—N15 | 119.78(3) |
| C3—C4—C10 | 119.23(3) | C7—C8—C9 | 118.07(2) |
| C3—C4—C23 | 120.70(3) | C7—C8—C18 | 120.12 (3) |
| C4—C10—C9 | 118.68(3) | C7—C6—C12 | 118.49(2) |
| C4—C10—C5 | 124.12(2) | C8—C9—C10 | 123.37(2) |
| C5—C6—C7 | 119.83(3) | C8—C18—C17 | 109.18(3) |
| C5—C6—C12 | 121.67(2) | C9—C8—C18 | 121.80(3) |
| C5—C10—C9 | 117.19(3) | C10—C4—C23 | 120.07(2) |
| C6—C5—C10 | 121.64(3) | C12—C13—C14 | 108.60(3) |
| C6—C7—C8 | 119.86(3) | C16—C17—C18 | 109.85(2) |
| C6—C12—C13 | 108.76(2) | C17—C16—N15 | 111.94(2) |

**Figure S1.** Analysis of observed $\Delta\rho$ *vs.* expected $\Delta\rho$.

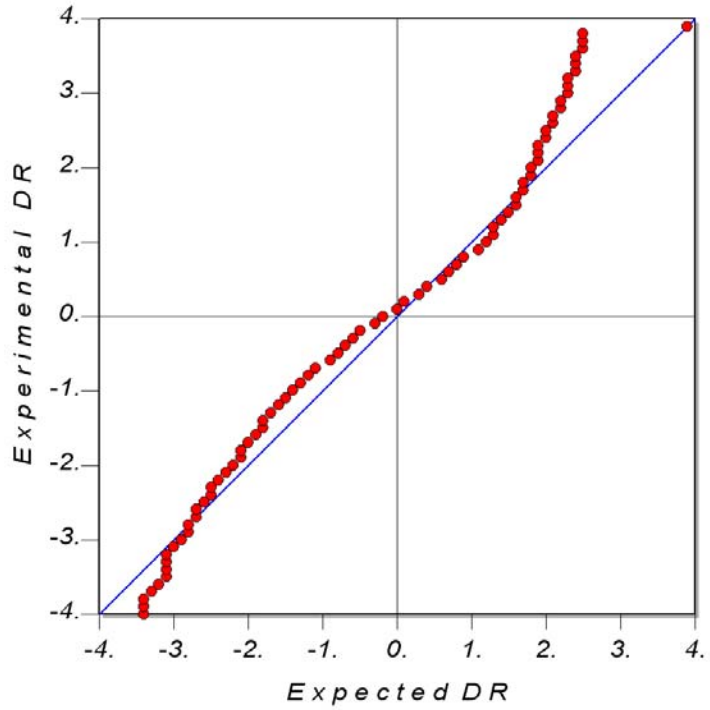



**Figure S2.**
Analysis of observed and calculated structure factors as a function of reciprocal resolution. .

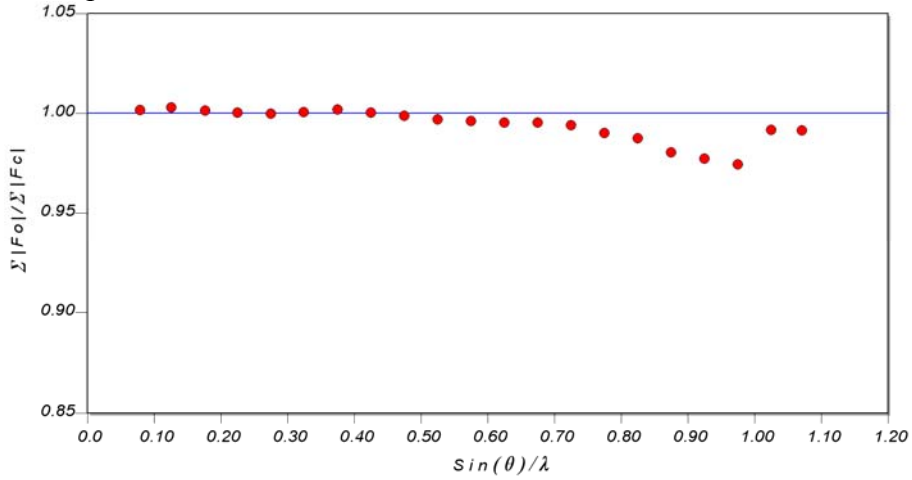


**Figure S3**. Residual Fourier electron density map of C-102 dye in the chromen-2-one plane after ELMAM2 refinement. Contours ±0.05e/Å$^3$.
The map was computed up to $\sin\theta/\lambda$=0.8Å$^{-1}$.

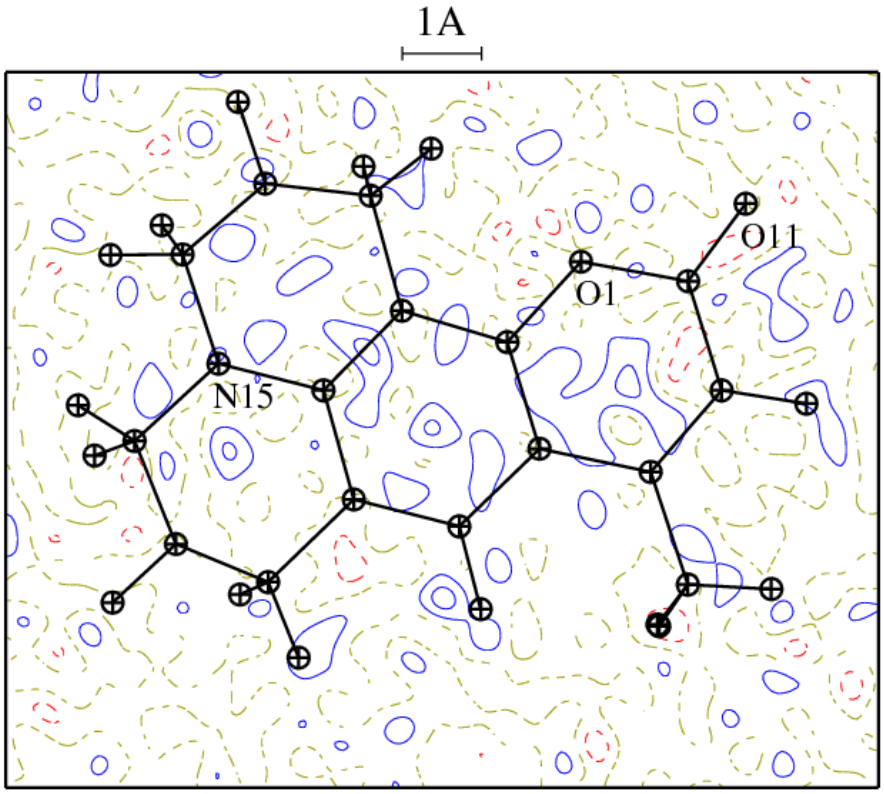
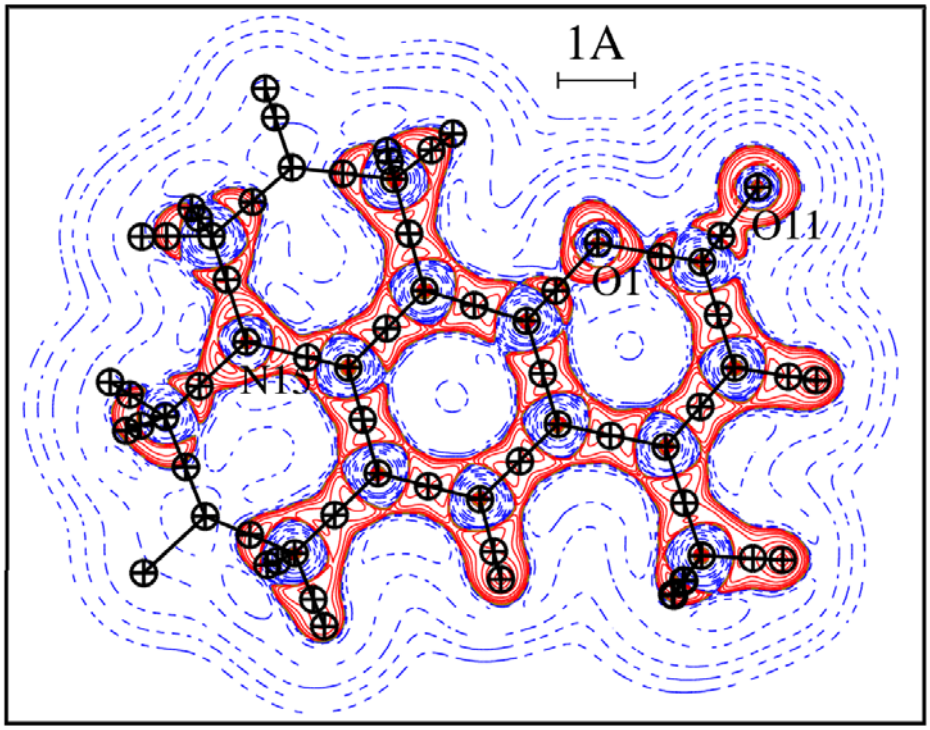


**Figure S4**: (a) Laplacian of the total electron density from the ELMAM2 model shown in the chromen-2-one ring system plane. (b) Difference of Laplacian ELMAM2 – EXPML. Contours ±0.01 e/Å$^5$. Blue contours indicate positive region; red, negative regions. Bonds critical points are also shown.

(a)




(b)